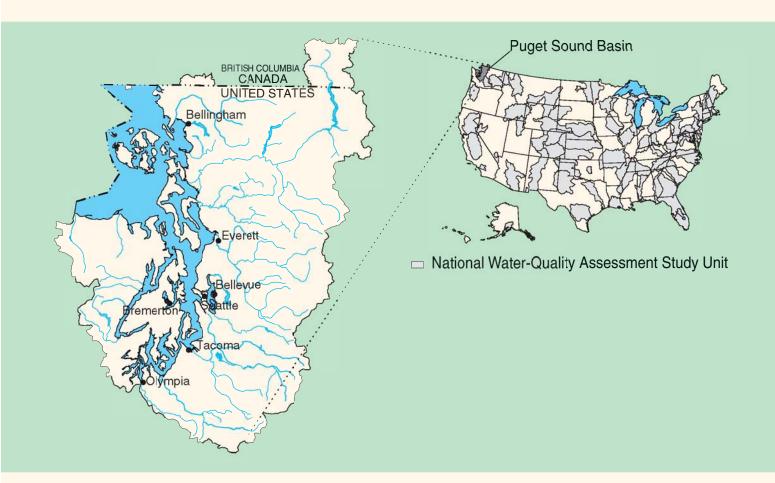


Surface-Water Quality of the Skokomish, Nooksack, and Green-Duwamish Rivers and Thornton Creek, Puget Sound Basin, Washington, 1995-98

By S.S. Embrey and L.M. Frans



U.S. GEOLOGICAL SURVEY Water-Resources Investigations Report 02-4190

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NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Tacoma, Washington 2003

U.S. DEPARTMENT OF THE INTERIOR

GALE A. NORTON, Secretary

U.S. GEOLOGICAL SURVEY

Charles G. Groat, Director

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FOREWORD

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources. Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity and quality, even more critical to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues. NAWQA results can contribute to informed decisions that result in practical and effective waterresource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings.

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for costeffective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, nongovernment organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch Associate Director for Water

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CONVERSION FACTORS AND VERTICAL DATUM

CONVERSION FACTORS

Multiply	Ву	To obtain
	Length	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
foot (ft	0.3048	meter
inch (in)	25.4	millimeter
mile (mi)	1.609	kilometer
pound, avoirdupois (lb)	0.4536	kilogram
pound per day (lb/d)	0.4536	kilogram per day
square mile (mi ²)	2.590	square kilometer
ton per year (ton/yr)	0.9072	metric ton per year

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F=1.8 °C+32.

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows: °C=(°F-32)/1.8.

Chemical concentrations in water are given in milligrams per liter (mg/L) or micrograms per liter (μ g/L). Milligrams per liter is a unit expressing the solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, milligrams per liter is equivalent to "parts per million" and micrograms per liter is equivalent to "parts per million" and micrograms per liter is equivalent to

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μ S/cm at 25°C).

VERTICAL DATUM

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Altitude, as used in this report, refers to distance above or below sea level.

Surface-Water Quality of the Skokomish, Nooksack, and Green-Duwamish Rivers and Thornton Creek, Puget Sound Basin, Washington, 1995-98

S.S. Embrey and L.M. Frans

ABSTRACT

Streamflow and surface-water-quality data were collected from November 1995 through April 1998 (water years 1996-98) from a surface-water network in the Puget Sound Basin study unit of the U.S. Geological Survey National Water-Quality Assessment program. Water samples collected monthly and during storm runoff events were analyzed for nutrients, major ions, organic carbon, and suspended sediment, and at selected sites, samples were analyzed for pesticides and volatile organic compounds. Eleven sites were established in three major watersheds-two in the Skokomish River Basin, three in the Nooksack River Basin, five in the Green-Duwamish River Basin, and one site in Thornton Creek Basin, a small tributary to Lake Washington. The Skokomish River near Potlatch, Nooksack River at Brennan, and Duwamish River at Tukwila are integrators of mixed land uses with the sampling sites locally influenced by forestry practices, agriculture, and urbanization, respectively. The remaining eight sites are indicators of relatively homogeneous land use/land cover in their basins. The site on the North Fork Skokomish River is an indicator site chosen to measure reference or background conditions in the study unit. In the Nooksack River Basin, the site on Fishtrap Creek is an indicator of agriculture, and the Nooksack River at North Cedarville is an indicator site of forestry practices in the upper watershed. In the Green-Duwamish River Basin, Springbrook Creek is an urban indicator, Big Soos Creek is an indicator of a rapidly developing suburban basin; Newaukum Creek is an indicator of agriculture; and the Green River above Twin Camp Creek is an indicator of forestry practices. Thornton Creek is an indicator of high-density urban residential and commercial development.

Conditions during the first 18 months of sampling were dominated by above-normal precipitation. For the Seattle-Tacoma area, water year 1997 was the wettest of the 3 years during the samplecollection period. Nearly 52 inches fell (about 14 inches above average) and monthly precipitation was often 200 percent of normal. The wet years kept streamflows generally above normal and contributed to high concentrations of pesticides, nutrients, suspended sediment, and organic carbon in samples.

On the basis of chemical concentrations, dissolved oxygen concentrations, and water temperature, the relative quality of water among the 11 study sites ranged from exceptionally high in the North Fork Skokomish and the Green to fair in Springbrook and Thornton. Water in the large rivers (Skokomish, Nooksack, Green-Duwamish) and in two of the small streams in the Puget Sound Lowlands (Big Soos and Newaukum) was characterized by dilute water chemistry with dissolved solids concentrations less than 130 milligrams per liter. Water in three other small streams in the Lowlands (Fishtrap, Springbrook, and Thornton) had dissolved solids concentrations as high as 320 milligrams per liter. Nutrient and pesticide concentrations mostly were higher in the small streams than in the large rivers. Suspended-sediment concentrations, however, were highest in the large rivers, with averages ranging from 85 to 443 milligrams per liter. During storm and flood events, suspended-sediment concentrations in samples from the Nooksack were as much as 2,800 milligrams per liter, and from the Skokomish, 1,500 milligrams per liter.

Out of 86 pesticides and 86 volatile organic compounds analyzed, a total of 35 pesticides and 11 volatile organic compounds were detected at concentrations above laboratory reporting levels in samples collected from the four intensively studied sites, the lower Nooksack River, Duwamish River, Fishtrap Creek, and Thornton Creek. Herbicides were detected more frequently than insecticides. The herbicide prometon was detected in 66 percent of all 124 samples collected, followed by simazine (65 percent), atrazine (64 percent), and the insecticide diazinon (50 percent). The detected volatile organic compounds belonged to one of three general classes fuel-related, the trihalomethanes, or solvents.

Water-quality standards and criteria for drinking water or for the protection of aquatic life were nearly always met, except on occasion by concentrations of dissolved oxygen, iron, and manganese in samples from Springbrook and Fishtrap, and concentrations of diazinon in Thornton and Fishtrap. Concentrations of three other insecticides (carbaryl, chlorpyrifos, and lindane) also did not meet criteria protecting aquatic life in a few samples (from 1 to 5) from Thornton and Fishtrap and from the Duwamish River.

Water-quality conditions at the sampling sites resulted from natural characteristics of the watersheds and from human activities. In the Nooksack and Skokomish, natural conditions were probably important contributors to the large suspended-sediment concentrations observed during high streamflow events. However, logging and road building in the basins might also have contributed to the suspendedsediment loads. In the forested study basins, the water chemistry was more dilute, based on dissolved solids and nutrient concentrations. The North Fork Skokomish (indicator site of background conditions) and the Green (indicator site of forestry and natural conditions) were characterized by high-quality water with low concentrations of dissolved solids, nutrients, and sediment and by standards or criteria that were nearly always met. Unlike the high-quality water at the background and forestry sites, natural conditions appear to have adversely affected the quality of water in Springbrook. High concentrations of iron and manganese and low dissolved-oxygen concentrations were possibly the result of ground-water discharge at this site.

Of all the sites, nutrient concentrations were highest in the agricultural streams (Fishtrap and Newaukum) and next highest in the urban streams, indicating that human activities affect the water quality of these streams. Of the three large rivers integrating a mix of land uses, the lower Nooksack, in an agricultural setting, on average had the highest total nitrogen and phosphorus concentrations, followed by the Duwamish in an urban setting, and the Skokomish in a forestry-practices setting.

In both urban and agricultural settings, pesticides affected water quality at the four sites sampled for organic compounds. However, more types of pesticides were found at the agricultural sites than at the urban sites. The most pesticides were detected in Fishtrap. Many of these were pesticides applied for agricultural purposes, but several were pesticides applied in urban settings, such as those used in maintaining rights-ofway. In urban Thornton Creek, however, high application rates and retail availability of pesticides likely resulted in generally higher concentrations, the detections of certain pesticides in many samples year round, and the number of times insecticide concentrations did not meet chronic criteria for the protection of freshwater aquatic life.

The two sites located in urban areas also had more detections of volatile organic compounds and at a higher detection frequency than the two sites in agricultural areas. The most compounds were detected in Thornton, and in the highest concentrations. Conversely, the least number of compounds was detected in the lower Nooksack, with only 2 percent urban land upstream. Methyl tert-butyl ether, an automotive fuel additive, was detected in a few samples from Fishtrap. Many solvents, such as trichloroethene and tetrachloroethene, were detected only in samples from the urban sites on the Duwamish River and Thornton Creek. The only volatile organic compound with a distinctly agricultural signature was 1,2dichloropropane, detected only in Fishtrap Creek samples.

INTRODUCTION

The U.S. Geological Survey (USGS) began the National Water-Quality Assessment (NAWQA) program in 1991, with hydrologic data collection at 20 study units throughout the United States. NAWQA study units across the nation, using consistent sampling and analytical methods, contribute data and information on surface- and ground-water quality, bedsediment quality, ecology, biology, and land use to the program's database. These data are being used to describe the status and trends in the quality of the Nation's surface- and ground-water resources and to identify the major natural and human factors affecting water quality (Leahy and others, 1990; 1993). Surfacewater investigations in the study units have several objectives, including descriptions of the occurrence and spatial distribution of water-quality constituents, information on the seasonal variation and frequency of occurrence of selected water-quality constituents at key locations, and estimation of loads of selected waterquality constituents (Hirsch and others, 1988). During the first, high-intensity phase (HIP) of study in each study unit, the focus is on the assessment of occurrence and distribution (Gilliom and others, 1995).

In 1994, studies began in another 16 study units, one of which is the Puget Sound Basin in Washington State. Land use and habitat vary greatly in the Puget Sound Basin study unit, ranging from remote, forested mountain areas to intensively farmed agricultural regions or densely populated urban centers. However, about 70 percent of Washington State's population lives in the region, making the study unit a representative of urban conditions for the NAWQA program. Surface-water investigations in the Puget Sound Basin study unit began in 1995 with analyses of historical data largely collected by State and county agencies. This retrospective work included analysis of surface-water-quality data collected during 1980-93 (Embrey and Inkpen, 1998), biological data collected through 1995 (Black and Silkey, 1998), and pesticide data collected during 1987-95 (Bortleson and Davis, 1997).

Purpose of Report and Scope of Study

This report presents the results of field measurements and laboratory analyses of watercolumn samples collected from the surface-water fixed-site sampling network of the Puget Sound Basin study unit of NAWQA. Data for the study unit are summarized, related to water-quality criteria, standards, or guidelines, and discussed in detail for each site in the sampling network. Temporal variations in hydrology and water quality, relations of stream conditions to land use, and transport of selected constituents are also discussed.

The scope of work included monthly watersample collections at 11 sites, with additional sampling during storm-runoff and high-flow events. Sample collection at all 11 sites began in March 1996 and continued through April 1998. Some storm-runoff samples were collected at selected sites during November 1995-February 1996 prior to the HIP. Data collection included continuous monitoring of streamflow, specific conductance, water temperature, and dissolved-oxygen concentration, and water samples for measurements of physical properties, chemical-constituent concentrations (nutrients, major ions, and organic compounds), and suspendedsediment concentrations. The water-quality data for the study can be obtained from the NAWQA web site at URL http://water.usgs.gov/nawqa/.

Acknowledgments

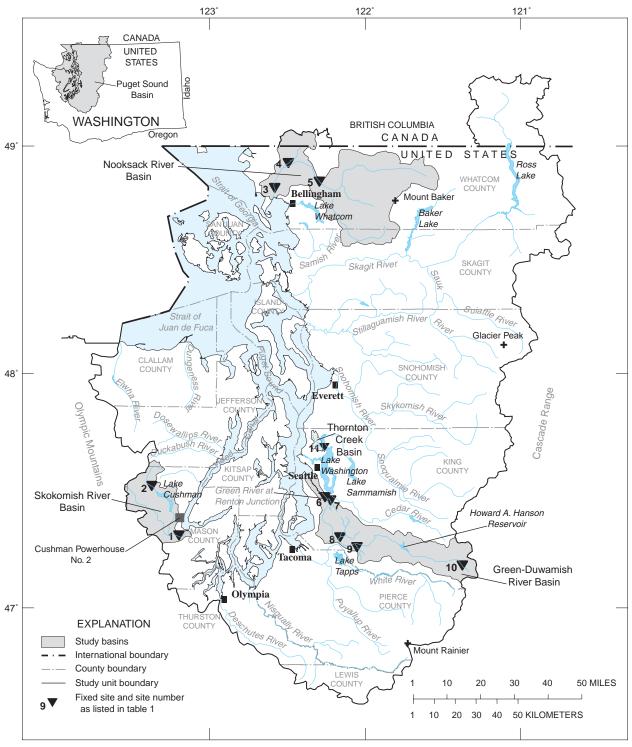
The authors would like to thank all the Puget Sound Basin NAWQA team members and Washington District Office personnel for their numerous contributions and assistance during the samplecollection, data-management, and report preparation phases of the past several years. We would like to express great appreciation for Lead Hydrologic Technician Kathleen Greene for her work in overseeing much of the effort and preparations required for field work, including ordering and maintaining supplies and equipment, data collection, basic-data records management, and her willingness to participate in all the pre-dawn storm sampling. The authors also thank Joseph Gilbert, a critical member of the field-collection teams, for his enthusiasm and diligence in quickly learning the techniques required for streamflow data collection and water-quality sampling and processing, and to Brett Smith of the Spokane office for his role in establishing monitoring stations at the beginning of the high-intensity phase of data collection, mentoring other team members in various aspects of data analysis and management, and participating in much of the field work during the study. Several others who were instrumental in the successful collection of monthly sample collections and the oftentimes difficult stormevent samples are noted here— James Ebbert, Gary Holloway, Emily Inkpen, Gregory Justin, Moon Kim, and Ward Staubitz. In addition to her database management tasks for the District Office, Stephanie Leisle provided assistance in sampling during storms and synoptic studies. We wish also to express our gratitude to Frank Voss and Alan Haggland for their work in managing the project's databases and their work with geographic information systems in land-use analyses, and for Alan's summaries of quality-control data; to David Kresch for analysis of surface-water data in the Green-Duwamish River Basin and the construction of data sets of daily flows for the Duwamish River and Springbrook Creek; and to Ginger Renslow, Deanna Walth, and Judith Wayenberg for preparation of the manuscript and illustrations for publication and for editorial assistance.

Description of the Puget Sound Basin Study Unit

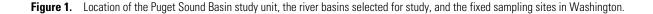
The Puget Sound Basin (PSB) study unit encompasses the 13,700-mi² (square mile) area that drains to Puget Sound and adjacent marine waters. The area includes all or part of 13 counties in western Washington, as well as the Skagit River headwaters and part of the Nooksack River Basin in the province of British Columbia, Canada (fig. 1). Staubitz and others (1997) described in detail the environmental setting and the implications of natural and human factors on surface- and ground-water resources in the study unit.

The Cascade Range bounds the study unit on the east and the Olympic Mountains of the Coastal Range bound the study unit on the west. Parts of these two mountain ranges and the Puget Sound Lowlands in between are included within the study boundaries of the PSB. The crest of the Cascade Range averages about 7,500 feet in altitude and includes the three volcanoes Mount Baker, Glacier Peak, and Mount Rainier, with altitudes ranging from 10,541 feet to 14,410 feet. The crest of the Olympic Mountains averages about 3,000 feet. Land-surface altitude of the Puget Sound Lowlands is generally less than 600 feet.

The PSB has a Pacific Coast marine climate characterized by cool, wet winters and warm, dry summers. Average annual air temperatures in the Lowlands range from 50 to 60°F (degrees Fahrenheit). In winter in the Lowlands, daily temperatures rarely fall below freezing; and in summer, daily highs range between 70 and 85°F. About 80 percent of the annual precipitation falls during the wet season, which begins in October and extends through April. In the Lowlands, annual precipitation falls mostly as rain, averaging about 40 inches per year and ranging from 16 to 47 inches per year. In the mountains, precipitation averages about 90 inches per year and ranges from 60 to more than 200 inches per year depending on altitude and orientation to prevailing storm patterns (Staubitz and others, 1997).



Base from U.S. Geological Survey digital data, 1:2,000,000, 1972 Albers Conic Equal-Area Projection Standard parallels 47* and 49*, central meridian 122*



Fourteen major rivers and numerous minor streams drain to Puget Sound and adjacent marine waters. The major rivers, with headwaters in the mountains, account for more than 91 percent of the $52,500 \text{ ft}^3/\text{s}$ (cubic feet per second) of mean annual surface-water inflow to the study unit's marine waters (Williams, 1981; Staubitz and others, 1997). High flows in streams are typical during late October through February because of winter rainfall. In the major river basins with high-altitude headwaters, flows continue to be high through June because of snowmelt. Low flows typically occur in all PSB streams during August and into September. Flows in some streams are also influenced by glaciers or large snow fields in the headwaters and by flow regulation at dams and reservoirs. In several small basins in the Puget Sound Lowlands, Vaccaro and others (1998) indicate that more than 70 percent of ground-water recharge eventually discharges to streams as baseflow and can make up more than 50 percent of the streamflow. In large river basins such as the Nooksack River Basin, about 80 percent of ground-water recharge eventually discharges to the rivers.

About 3.7 million people, or 70 percent of the population of Washington State, live in the PSB. Most of these people (98 percent) live within 20 miles of the Puget Sound shoreline in an urban corridor that includes the cities of Seattle, Tacoma, Bellevue, and Everett (Staubitz and others, 1997). Between 1970 and 1990, the population grew by about 37 percent, or nearly 1 million people. By 2010, the region is expected to gain another 1.1 million people (Staubitz and others, 1997).

The three principal types of land use/land cover in the PSB study unit are forest, urban, and agriculture. Forest land covers about 74 percent, agriculture nearly 6 percent, and urban development about 9 percent. The balance is covered by rangeland, water, tundra, glaciers, wetlands, and barren land. In each of the major river basins, forests make up more than one-half the land cover. Typically, forests cover the basins mostly in the uplands and mountains, whereas urban and agricultural land uses are concentrated in the Lowlands. Most major drainages have some agricultural land-use areas, which tend to be restricted to the alluvial river valleys.

Fixed-Site Sampling Network Design

NAWQA program study designs vary, depending on the basin. Some designs established a fixed-site monitoring network within one large river basin consisting of the mainstem and its tributary systems. The multiple river basins that make up the PSB study unit, however, called for a different design to establish a network meeting study-unit and national goals. Landuse/land-cover and other ancillary data allowed a conceptual stratification of the PSB study unit so that rivers draining to Puget Sound are represented by three general basin types: (1) rivers draining the Olympic Mountains with predominantly forested watersheds, (2) rivers draining the Cascade Range-Puget Sound Lowlands with forested upper watersheds and agricultural or urbanized lower watersheds, and (3) small streams draining the Puget Sound Lowlands with watersheds that are mostly urban, agricultural, forested, or a combination (W.W. Staubitz, U.S. Geological Survey, written commun., December 5, 1995).

Three major basins and their tributaries were then selected to represent the three study-unit strata types and, therefore, the general range of conditions observed within the PSB. The Skokomish River Basin represents type 1; the Nooksack and Green-Duwamish River Basins represent type 2; and the Lowlands tributaries to these rivers represent type 3. The Thornton Creek Basin also represents a type 3 basin. The three major basins generally represent large-scale study unit conditions with mixes of features and contain tributaries representing small-scale conditions with relatively homogeneous features such as land use/land cover. Together, the large-scale basins and their tributaries can provide an integrated watershed assessment.

The fixed-site network for the PSB study unit consisted of 11 sites where surface-water samples were routinely collected. Two sites were established in the Skokomish River Basin, three in the Nooksack River Basin, five in the Green-Duwamish River Basin, and one site in the Thornton Creek Basin (fig. 1). NAWQA fixed sites fall into two general types of sitesintegrator or indicator. Integrator sites in the PSB represent mixed water-quality conditions in large basins consisting of a variety of land-use and human and natural influences. Although water quality at the integrator sites is influenced by a large part of the drainage basin, the site location was generally in a setting predominantly influenced locally by forestry practices, agriculture, or urbanization. In contrast, water quality at indicator sites reflects conditions in basins with relatively homogeneous land use. For the PSB, 3 of the 11 sites, Skokomish River near Potlatch, Nooksack River at Brennan, and Duwamish River at Tukwila, are integrator sites located near the mouths of their respective basins. The remaining eight sites are indicator sites, seven of which are on tributaries within the three representative river basins. One site, Thornton Creek near Seattle, is on a small tributary stream draining into Lake Washington (fig. 1, table 1).

In the Skokomish River Basin, site 1 on the Skokomish River near Potlatch is an integrator site with influences from forestry practices occurring within the South Fork Skokomish River Basin. Site 2 on the North Fork Skokomish River (NF Skokomish) is a reference indicator site chosen to indicate background conditions in the study unit. The basin upstream of this site is located within the Olympic National Park and is relatively undisturbed.

In the Skokomish River Basin, site 1 on the Skokomish River near Potlatch is an integrator site with influences from forestry practices occurring within the South Fork Skokomish River Basin. Site 2 on the North Fork Skokomish River (NF Skokomish) is a reference indicator site chosen to indicate background conditions in the study unit. The basin upstream of this site is located within the Olympic National Park and is relatively undisturbed.

In the Nooksack River Basin, site 3 on the Nooksack River at Brennan (lower Nooksack) is an integrator site influenced by intensive agriculture upstream from the sampling site. Site 4, located on Fishtrap Creek, represents an intensively farmed (row crops, dairy, and poultry) tributary basin with some urban influences from part of the basin in Canada and the nearby city of Lynden. A second site located on the mainstem Nooksack River at North Cedarville (upper Nooksack, site 5) is an indicator of forestry practices in the upper watershed. This site also functions as an integrator site by integrating the water quality of the three major forks of the Nooksack River (North, Middle, and South Forks) whose drainages consist of undisturbed headwaters, logging, some agricultural activities, and glacial meltwater conditions.

In the Green-Duwamish River Basin, site 6 on the Duwamish River at Tukwila is an integrator site with urban influences near the site. Four sites, one on each of four tributaries, represents conditions, typical of the urban-suburban settings in the PSB. Site 7 on Springbrook Creek is an indicator of commercial, light industrial, and residential land use; site 8 on Big Soos Creek is an indicator of a rapidly developing suburban basin: site 9 on Newaukum Creek is an indicator of hobby-farm agriculture that includes gardens, horses, and llamas, and cattle and dairy agriculture. Site 10 on the Green River above Twin Camp Creek (upper Green) is an indicator of forestry practices as well as conditions in the uppermost parts of basins with headwaters in the mountains. Site 11 on Thornton Creek is an indicator of long-established, high-density residential and commercial development in the north Seattle metropolitan area.

The fixed sites are further classified as basic and intensive according to the type and degree of monitoring. Basic fixed sites characterize the spatial and temporal distribution of general water-quality conditions and constituent transport in relation to hydrologic conditions and contaminant sources (Gilliom and others, 1995). Streamflow, specific electrical conductance (conductivity), and in some cases dissolved-oxygen concentrations, were continuously monitored. Water samples were collected on a monthly fixed-interval schedule and over a range of storm or high-flow events for at least 2 years. Waterquality properties (water temperature, pH, conductivity), concentrations of alkalinity and bicarbonate, and concentrations of major constituents (major ions, nutrients), organic carbon, and suspended sediment were analyzed for in these water samples.

Table 1. Description of surface-water-quality fixed sampling sites in the Puget Sound Basin study unit, Washington

[Basic monitoring level included monthly and storm sampling for field parameters, basic inorganic chemistry, and suspended sediment. Intensive monitoring level consisted of the basic monitoring sampling frequency and water-quality analyses plus pesticide and volatile organic compound analyses]

River basin	Site No.	Station No.	Station name	Percentage of land use/land cover in basin				Monitoring	Site type–land use/land cover ordered from	Drainage area
				Urban	Agri- culture	Forest	Other	level	nearest to most distant from the site	(square miles)
Skokomish	1	12061500	Skokomish River near Potlatch	0.3	1.5	97.5	0.7	Basic	Integrator-forestry practices, some agriculture	¹ 227
Skokomish	2	12056500	North Fork Skokomish River below Staircase Rapids near Hoodsport	0	0	89.3	10.7	Basic	Indicator-Reference	57.2
Nooksack	3	12213140	Nooksack River at Brennan	3	16.4	72.6	8	Intensive	Integrator–agriculture, forestry practices, some urban	790
Nooksack	4	12212100	Fishtrap Creek at Flynn Road at Lynden	15.1	72.1	12.8	0	Intensive	Indicator–agriculture (row crop, dairy), some urban	38.1
Nooksack	5	12210700	Nooksack River at North Cedarville	.8	1.2	88.2	9.8	Basic	Indicator–forestry practices, some agriculture	589
Green/ Duwamish	6	12113390	Duwamish River at Golf Course at Tukwila	20.9	6.5	71.1	1.5	Intensive	Integrator–urban, mixed agriculture, forestry practices	461
Green/ Duwamish	7	12113375	Springbrook Creek at Tukwila	72.7	19.8	0.5	7	Basic	Indicator–urban (commercial, light industry, residential)	20
Green/ Duwamish	8	12112600	Big Soos Creek above Hatchery near Auburn	49.9	2.2	45.2	2.6	Basic	Indicator–suburban, urban	66.7
Green/ Duwamish	9	12108500	Newaukum Creek near Black Diamond	22.7	36.1	40.6	.6	Basic	Indicator–agriculture (hobby farms, dairy)	27.4
Green/ Duwamish	10	12103380	Green River above Twin Camp Creek near Lester	0	0	100	0	Basic	Indicator-forestry practices	16.5
Thornton	11	12128000	Thornton Creek near Seattle	100	0	0	0	Intensive	Indicator–urban (high- density residential, commercial)	12.1

¹Includes 99 square miles of the North Fork Skokomish Basin that are noncontributing most of the year.

Intensive fixed sites are a subset of the basic fixed sites. In addition to analyses listed above for basic fixed sites, data were collected from intensive fixed sites to characterize seasonal and short-term temporal variability in general water quality as well as the occurrence and seasonal patterns in concentrations and transport of pesticides and volatile organic compounds (VOCs). Pesticides and VOCs were analyzed for in water samples from these sites for at least 1 year. Continuous monitoring, fixed-interval monthly sampling, and storm-event sampling were the same as those listed above for basic fixed sites, and some additional high-frequency sampling was scheduled during selected seasons.

METHODS OF SAMPLE COLLECTION AND ANALYSIS

This section presents an overview of standard USGS and NAWQA procedures governing sample collection, handling, and analysis in the field and in the laboratory. Detailed protocols and analytical methods can be found in the publications cited in the following paragraphs, some of which can be accessed on-line at the URLs http://water.usgs.gov/,

http://wwwnwql.cr.usgs.gov/Public/ref_list.html, and http://wwwnwql.cr.usgs.gov/Public/nwql_memo.html.

Water-Sample Collection, Field Procedures, and Sample Preparation

The use of standard USGS sampling equipment, cleaning of equipment in preparation for the field, and the collection, processing, and handling of water samples generally followed the protocols and guidelines described in Ward and Harr (1990), Shelton (1994; 1997), Sandstrom (1995), and Horowitz and others (1994). All samples were processed, preserved, and prepared for shipment, and all field determinations were completed while at the study site except for the processing of filtered sample water for pesticides by solid-phase extractions (SPE). The sample water for pesticide analyses was extracted at the District's Field Services Unit (FSU) laboratory within 1 or 2 days after sample collection, as allowed by the protocols. The cone splitter and all bottles used to collect stream water, to receive water poured through the cone splitter, and to be filled for laboratory analyses were rinsed thoroughly with native water prior to collection and processing.

For the major constituents and water-quality properties, samples were collected from multiple verticals spaced in equal-width increments using depthintegrating DH-81 or epoxy-coated D-77 samplers (Ward and Harr, 1990). Depth- and width-integrating techniques result in a discharge-weighted, composite water sample representative of the stream's chemistry. Flood-stage flows sometimes required deviations from these protocols, either by using a D-77 equipped with a bag sampler or by reducing the number of sampling verticals, or both. If pesticides were to be analyzed, Teflon collection bottles and nozzle assemblies were used; otherwise, polypropylene bottles and nozzles were used.

For VOCs and organic carbon, water samples were collected at a single vertical in the center flow of the stream. Water for VOCs analysis was collected directly into 40-mL (milliliter) vials contained in a weighted, stainless-steel sampler (Shelton, 1997). While completely submerged, the sampler allows the vials to be filled by gentle air displacement without aeration. After several minutes, the sampler was removed from the stream, the vials carefully removed, and the sample preserved by acidification with 1:1 hydrochloric acid/water solution to a pH between 1.7 and 2.0 standard units. The organic carbon sampler is also a weighted sampler, which holds an open bottle that fills when lowered beneath the water surface. The vials for VOCs and organic carbon samples were then shipped with the nutrient samples on ice to the National Water Quality Laboratory (NWQL) in Arvada, Colo.

A Teflon cone splitter was used to achieve a final composite water sample for field measurements and for laboratory analyses of nutrients, major ions, pesticides, and suspended sediment (Capel and Larson, 1996). All the water collected with the D-77 or DH-81 sampler at the verticals was poured through the cone splitter into receiving bottles made of Teflon if pesticide analyses were involved or made of polypropylene if only inorganic analyses were to be done. Sub-samples for specific laboratory analyses requiring whole water (total phosphorus and total ammonia-plus-organic nitrogen concentrations) were obtained by pouring one or more of the receiving bottles containing composited water back through the cone and capturing the volumes from this second split into a specific bottle required by the NWQL. The composited water in the remainder of the receiving bottles was then used for measurements of pH and conductivity on whole water and for laboratory analyses requiring filtered water.

After splitting, sample water for analyses of selected dissolved nutrients and dissolved major ions was filtered through a polypropylene-encapsulated filter having a 0.45-µm (micrometer) pore size. For dissolved pesticides, water was filtered through a 142-mm (millimeter)-diameter, 0.7-µm baked, glassfiber filter on an aluminum filter holder (Sandstrom, 1995). For dissolved and suspended organic carbon, water was collected directly into a baked glass bottle and filtered under nitrogen pressure through a 47-mmdiameter, 0.45-µm pore size silver filter held in a stainless steel filtration device. The filtrate was used for analysis of dissolved organic carbon (DOC), and the material retained on the filter was used for suspended organic carbon (SOC). Filtered water samples for cation analyses were preserved with nitric acid. The water for nutrient and organic carbon determinations was shipped on ice the same day of collection or the following morning for overnight delivery to the NWQL. All bottles for major-ion analyses, which do not require chilling, were either shipped with the chilled samples for convenience or held for a later mailing (typically no more than 1 week after sampling). The filtered water for pesticides was transported to the District's FSU laboratory on ice and refrigerated until extraction onto solid-phase media. The SPE cartridges were chilled and shipped the same day or within 1-2 days after extraction to the NWQL. Bottles for determining suspended-sediment concentrations were held at room temperature and out of direct light. At the end of each month the samples were shipped to the USGS sediment laboratory in Vancouver, Wash., for analysis using methods described by Guy (1969).

Field Measurements

Water temperature, dissolved-oxygen (DO) concentration, conductivity, pH, alkalinity, and bicarbonate concentration were measured on-site following procedures described by Shelton (1994). At the center flow vertical, water temperature and DO concentration were determined directly in the stream temperature with an electronic thermistor and DO with a meter and probe. Conductivity and pH were measured on unfiltered water composited through the concentrations were measured on filtered, composited water using incremental titration with a digital titrator and sulfuric acid.

Laboratory Analyses

Unless otherwise stated in this report, major-ion and nutrient constituents, and pesticide and pesticidetransformation compounds analyzed on filtered water, are defined to be dissolved and are referred to simply by name. The definition includes iron, manganese, phosphorus, orthophosphate phosphorus (hereafter, orthophosphate), nitrite nitrogen (hereafter, nitrite), nitrite-plus-nitrate nitrogen (hereafter, nitrate), and ammonia-plus-organic nitrogen (hereafter, organic nitrogen). The nutrients measured in whole water are referred to as total phosphorus and total ammonia-plusorganic nitrogen (hereafter, total organic nitrogen). VOCs, all analyzed on whole water, are reported as total recoverable concentrations and are referred to by their name only. Total nitrogen concentration in this report is the sum concentration of the different nitrogen species detected in a sample—nitrite, nitrate, ammonia, and total organic nitrogen.

At the NWQL, samples were analyzed for concentrations of nutrients by colorimetry (schedule 2702). Dissolved and total phosphorus and ammoniaplus-organic nitrogen were analyzed by a microkjeldahl digestion followed by colorimetry as described by Patton and Truitt (1992), and dissolved orthophosphate, and dissolved ammonia, nitrite, and nitrite-plus-nitrate nitrogen by procedures described in Fishman (1993). Major ions, iron, and manganese were analyzed by ion chromatography and inductively coupled plasma (schedule 2701) described by Fishman and Friedman (1989) and Fishman (1993). Suspended and dissolved organic carbon were analyzed by UVpromoted persulfate oxidation and infrared spectrometry (schedule 2075) using the methods of Wershaw and others (1987) and Brenton and Arnett (1993). Pesticides were determined by two methods: high-performance liquid chromatography (HPLC) by NWQL schedule 2051 (Werner and others, 1996) and gas chromatography-mass spectroscopy (GC/MS) by schedule 2010 (Zaugg and others, 1995; Lindley and others, 1996). The parameters included in each schedule and their associated laboratory minimum reporting levels or method detection limits (MRLs or MDLs) are given at the end of the report in Appendix A, tables A1 to A5.

Most of the samples for VOCs were analyzed using purge and trap capillary-column GC/MS by NWQL schedule 2020 (Rose and Schroeder, 1995; Connor and others, 1998). Prior to April 1996, the laboratory method (schedule 2090) analyzed for 59 compounds with a reporting limit of 0.2 μ g/L (micrograms per liter) (Rose and Schroeder, 1995). Only the first sample at each of the intensive fixed sites collected in March 1996 was analyzed using this method and no detections were reported. A new method was introduced in April 1996 that increased the number of analytes to 86 and lowered the reporting limits (Connor and others, 1998). From April 1996 to April 1997, the new VOC analytical method used MRLs that were usually set to censor (qualify) data at 0.05 or 0.1 μ g/L, but some were 5 µg/L or higher (Connor and others, 1998). In May 1997, the laboratory began censoring data at the laboratory reporting limit (LRL) (Connor and others, 1998; Childress and others, 1999). In samples where a compound was determined to be present, but at a concentration below the LRL or MRL, the concentration was quantified and qualified with a remark code of E (estimated). An analyte should be detected 99 percent of the time if its true concentration is equal to or greater than the LRL (Childress and others, 1999). Although the discussion in this report focuses on compounds that were detected at concentrations above the LRL, consideration is also given to compounds and concentration values as they were reported by the NWQL. A complete list of the LRLs for schedule 2020 can be found at the end of the report in Appendix A, table A6.

Collection and Analysis of Quality-Control Samples

Quality-control samples designed to measure bias and variability in the field included several types of blank samples, replicate samples, matrix-spiked replicate samples, and surrogate-compound spiked samples (Mueller and others, 1997). Field blanks monitor for possible contamination or bias within the sample-collection process and consist of subjecting analyte-free water to all aspects of normal sample collection, processing, and handling. Source-water blanks monitor for potential background concentrations of organic carbon or VOCs in the analyte-free water used to prepare field blanks and consist of pouring the analyte-free water directly into a collection bottle submitted to the laboratory for analysis. The canister blank monitors for potential contamination carry-over from the canister, which holds the analyte-free water for preparing the VOC field blank, to the VOC sampler. VOC trip blanks are used to determine if external VOCs from bottle handling and analytical processes, independent of the field sample processing scheme, are contaminating the samples. Replicate samples measure sampling and analytical variability. Split-replicate samples are subsamples of a single, larger sample and are used to characterize the reproducibility of sample processing

and the analytical process, and to produce multiple samples for spiking purposes. Concurrent-replicate samples are multiple samples collected nearly simultaneously in time and at the same location. Matrix-spiked replicate samples are used to measure interference or bias in the analytical results due to matrix effects. Field matrix-spiked replicate samples provide information about bias, analyte loss during shipping, and method performance for the analyses of pesticides and VOCs. Surrogate compounds are similar in physical and chemical properties to a target analyte, but are not normally found in environmental samples. Surrogate compounds added to pesticide samples (in the field) and to VOC samples (in the laboratory) are used to monitor analytical precision and accuracy. The results of the quality-control samples collected in the field as part of the study are summarized here and discussed at the end of the report in Appendix B and presented in tables B1 to B11 and in figure B1.

Quality-control samples in the laboratory are routinely analyzed as part of the quality-assurance plan described by Pritt and Raese (1995). These samples include standard reference materials, laboratory replicates, laboratory reagent blanks, spikes, and surrogates.

Field blanks for inorganic constituents were prepared with inorganic grade (IG) water obtained from the USGS Ocala (Florida) Field Services Unit where this water is quality assured for suitability in the testing of equipment and sampling in the field. Field blanks for pesticides and VOCs were prepared with pesticide grade (PG) water and volatile grade (VG) water, respectively, obtained from the NWQL where testing of lots showed the waters suitable for use in the field. Midway through the study, the NWQL changed the preparation method of the VG water. Prior to August 1997, the NWQL analyzed each lot of VG water by randomly selecting a few containers of the lot to check for the presence of VOCs prior to shipment to study units. Those lots with detections above the LRL were rejected. In August 1997, an additional procedure was introduced to remove any low-level VOCs present by purging each bottle of VG water with nitrogen gas (N_2) . VOCs found to be present in the VG water by the NWQL are listed in Appendix B at the end of the report. As discussed in Appendix B, blanks collected with the non-N₂ purged water had considerably more VOC detections than those collected with the N₂ purged water.

All field blanks were prepared at streamside by pouring blank water through the bottle-nozzle collection assembly and into the bottles used for subsequent sample collection. The blank water in the collection bottles was then poured through the cone splitter and subjected to all the same sample handling, processing, and preservation treatments as environmental samples. Field blanks for organic carbon were prepared by pouring PG or VG water into a baked 1-liter collection bottle, measuring a 100-mL or 200-mL aliquot in a glass graduated cylinder, and filtering this aliquot through a stainless-steel filtration device. The filtrate was analyzed for dissolved organic carbon, and material collected on the filter was analyzed for suspended organic carbon. Source-water blanks for organic carbon were prepared by pouring PG or VG water directly into a 125-mL baked glass bottle. Source-water blanks for VOCs were prepared by pouring the VG water directly into 40-mL vials, preserving with the same volume of acid used for environmental samples, then sealing and storing on ice for shipment. Canister blanks for VOCs were prepared by filling the canister with VG water and, grasping the vials with clean flask tongs, dipping the vials into the VG water. The field blank for VOCs was then prepared by submerging the sampler containing 40-mL vials into the canister, pouring in sufficient VG water to completely submerse the sampler, and allowing the sampler to fill the vials through the intake ports. The trip blanks were sealed vials of VG water prepared and shipped from the NWQL, taken to the field site alongside the vials to be used in collection, and then shipped back to the laboratory. A complete description of the quality-control program for surface-water samples can be found in Mueller and others (1997).

A total of 32 field blanks for major ions (table B1), 34 field blanks for nutrients (table B2), 30 field blanks for organic carbon (table B3), 9 field blanks for pesticides, and 16 field blanks for VOCs (table B4) were submitted to the NWQL during the period December 1995 to February 1998. In the field blanks, there were occasional detections of calcium, silica, nitrate, total phosphorus, orthophosphate, dissolved organic carbon, and a number of VOCs, but no detections of pesticides. No adjustments to the database were made on the basis of field blanks except for a period of time in September-October 1996 when values of methylbenzene (toluene) appeared to be affected by systematic contamination or positive bias. These methylbenzene values were coded with a V remark in the USGS database to prevent their inclusion in normal data retrievals for analysis and interpretation.

Variability in the chemical data was measured with 26 pairs of split replicate samples for major ions, 29 pairs for nutrients, and 5 pairs for pesticides; and with 20 pairs of concurrent replicate samples for dissolved organic carbon and 1 pair of concurrent replicate samples for VOCs. The amount of variability between samples was expressed as the relative percent difference in the concentrations. Relative percent differences for the major ion samples ranged from 0 to 58 percent, but median percent differences for each constituent were less than or equal to 6.0 percent (table B5). Relative differences between replicates of nutrient concentrations tended to be larger than for the major ions, ranging from 0 to 67 percent with median percent differences from 1 to 19 percent (table B6). Relative percent differences between replicates of organic carbon ranged from 0 to 40 percent with a median of 2.5 percent for dissolved, and from 0 to 100 percent with a median of 0 percent for suspended (table B7). For the pesticides, differences between replicates ranged from 0 to 40 percent, with median differences from 0 to 31 percent (table B8). The pair of VOC samples had identical concentrations of trichloromethane (chloroform), chloromethane (methyl chloride), 1-isopropyl-4-methylbenzene (p-isopropyltoluene), and 4-methyl-2-pentanone (methyl isobutyl ketone). The pair of methylbenzene concentrations differed by $0.01 \,\mu\text{g/L}$. No changes were made to any of the inorganic or organic chemical data sets on the basis of these replicate data.

In addition, no changes were made to any of the data sets on the basis of pesticide and VOC analyte recoveries in field-matrix- or surrogate-spiked samples, which is consistent with USGS standard practices (Paul Capel, Robert Gilliom, and Steven Larson, U.S. Geological Survey, written commun., 1996). Percent recoveries of the field-matrix-spike compounds were within a fairly narrow range (60-140 percent) for the schedule 2010 pesticides and the VOCs (Appendix B). Average recoveries for laboratory reagent spiked samples ranged from about 40 to 120 percent for the schedule 2010 pesticides and from 77 to 114 percent for the schedule 2020 VOCs. For schedule 2051 pesticides, however, low recoveries of 7 to 72 percent indicated that the reported concentrations of these analytes could be low and that a potential for false negatives existed.

Additional information and quality-control data are available from the Washington District USGS office in Tacoma, Washington. Information is also available on the World Wide Web at <u>http://wwwnwql.cr.usgs.gov/USGS/USGS_tech.html</u>, <u>http://water.usgs.gov/owq/quality.html/</u>, and <u>http://ca.water.usgs.gov/pnsp/rep/qcsummary</u>.

Streamflow Measurements

Instantaneous streamflow measurements for the time of sample collection were made according to standard USGS procedures (Rantz and others, 1982) or were determined from stage-discharge relations. Stagedischarge relations were mostly used for the Skokomish (site 1), NF Skokomish (site 2), and upper Green Rivers (site 10), and for Big Soos (site 8) and Newaukum Creeks (site 9). Combinations of measured streamflow or stage-discharge relations were used for Fishtrap (site 4) and Thornton Creeks (site 11). Occasionally, flows in Fishtrap Creek were affected by backwater when the Nooksack River was high. Daily streamflows for Fishtrap during these periods were estimated from gaged flows at an upstream site near the Canada-United States international boundary. Streamflows were measured for the upper Nooksack (site 5) or determined from stage-discharge relations from the nearby upstream gaging station, Nooksack River at Deming. Streamflows for the lower Nooksack (site 3) were obtained from stage-discharge relations at the upstream site, Nooksack River at Ferndale.

Gages were not established on the Duwamish (site 6) because of tidal influences nor on Springbrook (site 7) because of frequent backwater conditions. Instantaneous streamflows at these sites were measured on the day of sample collection and daily streamflows were estimated from nearby gages and drainage-area relations.

Loads and Yields

The transport (mass discharge) of a constituent past a monitoring site in a given amount of time is referred to as the load. Constituent loads for this report were estimated by the rating-curve method (Cohn and others, 1989; Crawford, 1991) using instantaneous sample concentration data and daily or unit streamflow data. Because some constituent concentrations included in this assessment were less than the detection limit, parameters of the rating curve were estimated by the maximum-likelihood method (Dempster and others, 1977; Wolynetz, 1979) or the linear attribution method (Chatterjee and McLeash, 1986). The Loadest2 computer program used to compute loads was selected for several reasons: the output includes estimates of annual and seasonal average constituent loads; the period of interest is user defined and not restricted to the calendar or water year; and with Aikaike's information criterion, the user can either specify a rating-curve equation or allow the program to choose among eight alternative forms of the rating curve for the best regression equation describing the data (Charles Crawford, U.S. Geological Survey, written commun., 1999). The program also provides an estimate of the daily load using the Beale ratio estimate, a simple estimate that does not include seasonal parameters (sine and cosine functions) or flow-based stratification (for example, loads calculated separately for low and high flows, then summed for a total load) (Crawford, 1996). For estimating uncertainty in the average loads obtained by the maximum-likelihood method, the program uses the method described by Likes (1980), which provides a minimum-variance unbiased estimate of the variance of a sum of lognormal variables, and by Gilroy and others (1990), which calculates the exact variance of average constituent loads obtained by the rating-curve method when the rating-curve parameters and residual-error variance are known with certainty. For estimating uncertainty with the linear-attribution method, the program uses the jackknife method (Efron, 1982), which is a robust method for examining sampling properties of a statistic with no requirement for distributional assumptions (Crawford, 1996). These methods and descriptions are detailed by Crawford (1996).

SURFACE-WATER-QUALITY OF THE SKOKOMISH, NOOKSACK, AND GREEN-DUWAMISH RIVERS AND THORNTON CREEK

This section presents the results of approximately 2 years of water-sample collection at the 11 fixed sites located within the Skokomish, Nooksack, and Green-Duwamish River Basins and Thornton Creek, and summarizes the study unit's hydrologic and water-quality conditions for the study period of water years 1996-98.

Sampling conditions during the first 18 months of the study were dominated by above-normal precipitation. During the last 8 months, conditions were drier: precipitation in November and December 1997 was about 50 percent of normal and early spring precipitation (February and April 1998) was also well below normal. The overall wet conditions resulted in many runoff events and flooding in large rivers and in small, lowland streams. These events contributed to detections of several kinds of pesticides and VOCs and to the presence of high concentrations of pesticides, nutrients, suspended sediment, and organic carbon.

Hydrologic Conditions—Climate and Streamflows

Puget Sound Basin weather for water year 1996 was wet, with temperatures about normal for the year. For the greater Seattle-Tacoma area, 50 inches of precipitation, about 12 inches above the average for the period of record, was recorded at the Seattle-Tacoma (SeaTac) International Airport weather station (Western Regional Climate Center, 1999) (fig. 2). Precipitation during the months of February, April, and December 1996 was about 200 percent of normal (fig. 3). During the last week of December and the first week of January, three major storms brought up to 2 feet of snow in places, followed by rising temperatures and heavy rains during the third storm. These three events combined for a total of 6.4 inches of precipitation (more than is normal for the entire month of December) and caused flooding and mud slides throughout the Seattle-Tacoma area.

The northern part of the study unit, represented by the weather station at Bellingham, and the western part, represented by the station at Shelton, were also wet during 1996 (fig. 2). The Bellingham station recorded 44 inches of precipitation, which is about 8 inches above the average for the period of record of 36 inches; the Shelton station recorded 85 inches, 20 inches above the average (Western Regional Climate Center, 1999).

Water year 1997 was the wettest of the 3 years spanning the period of sample collection; temperatures were again near normal, except during November when record highs were set. A total of 52 inches of precipitation, about 14 inches above average, fell over the Seattle-Tacoma area. A storm on March 18-20, 1997, was an event in which the jet stream delivered a plume of moisture-laden clouds from the warm, southwest Pacific Ocean into the Pacific Northwest, resulting in high volumes of rain. These winter storms frequently are rain-on-snow events, so coupled with heavy rainfall and snowmelt, extreme high flows and flooding can occur in PSB rivers. Peak flows for 1997 were recorded for many PSB rivers during this storm. From spring to fall 1997, monthly precipitation ranged from 230 percent to about 105 percent of normal (fig. 3). At the northern station in Bellingham, total precipitation was 48 inches, 13 inches above the average, and at Shelton, a total of 100 inches of precipitation fell, surpassing the average amount by 35 inches (Western Regional Climate Center, 1999).

Weather during water year 1998 was relatively dry and warm, compared with weather during 1996 and 1997 and with average conditions at the weather stations. Temperatures were above normal except during May and June. Record high temperatures were set on July 27 and 28, 1998. A total of 32 inches of precipitation, 5.8 inches below normal, was recorded at SeaTac International Airport. January and May were a little wetter than normal by 130 and 120 percent, respectively, but April was drier by 43 percent. Belownormal precipitation in June started the summer of 1998, which became the third driest summer on record (Western Regional Climate Center, 1999). Only 1.4 inches of rain fell during July, August, and September, compared to a normal of 3.8 inches. Precipitation recorded for the year at Bellingham and Shelton, 31 and 57 inches, respectively, was also below the averages for these weather stations (Western Regional Climate Center, 1999).

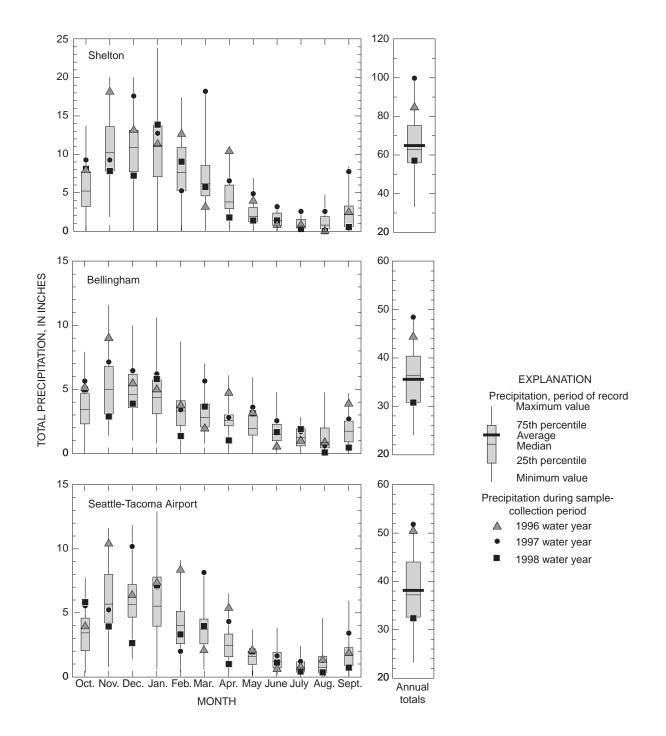


Figure 2. Distribution of monthly and annual precipitation for the period of record at Shelton, Bellingham, and Seattle-Tacoma International Airport, and total precipitation during the 1996–98 sample-collection period by month and for each year, for the Puget Sound Basin study unit, Washington.

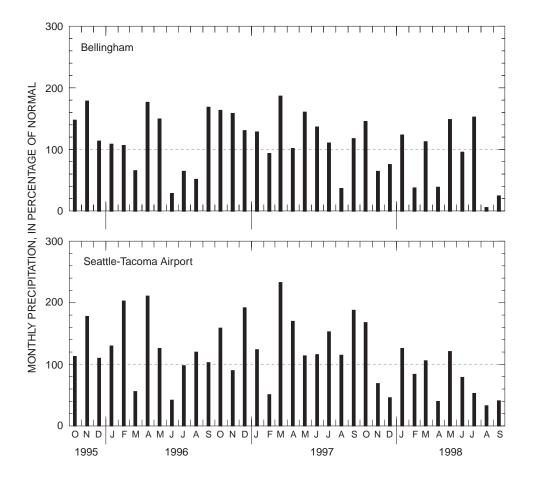


Figure 3. Departures of monthly precipitation from normal at Bellingham and Seattle-Tacoma Airport during the sample-collection period for the Puget Sound Basin study unit, Washington.

Snowpack in the mountains was above average in water year 1996; average to above average in 1997, depending on location; and near or below average in 1998, except in the Olympic Mountains where snowpack was above average (Wiggins and others, 1997, 1998, 1999). At the Cedar Lake National Weather Service station (altitude 1,560 feet) in the foothills of the Cascade Range, average total snowfall for the July through June period of record (referred to here as a winter year) was 71 inches. For winter year 1995-96, total snowfall was substantially below the average, amounting to only 46 inches, but total precipitation for the same period was 110 inches, about 10 inches above normal. During winter year 1996-97, however, the snowfall total was 86 inches, of which nearly 34 inches fell during December 1996. Snowfall during winter year 1997-98 was again well below the average with only 21 inches.

Annual streamflows at all the fixed sites having long-term gaging records were above average for water years 1996 and 1997 (fig. 4), due in part to aboveaverage snowpacks or to above-average precipitation. During 1997, the wettest year of the study period, annual streamflows in the Nooksack, Duwamish, and upper Green Rivers and in Big Soos and Newaukum Creeks were near recorded maximum flows for their respective periods of record. With a return to drier weather in 1998, streamflows were near or below average except for the Skokomish and NF Skokomish Rivers, in which streamflows remained above normal.

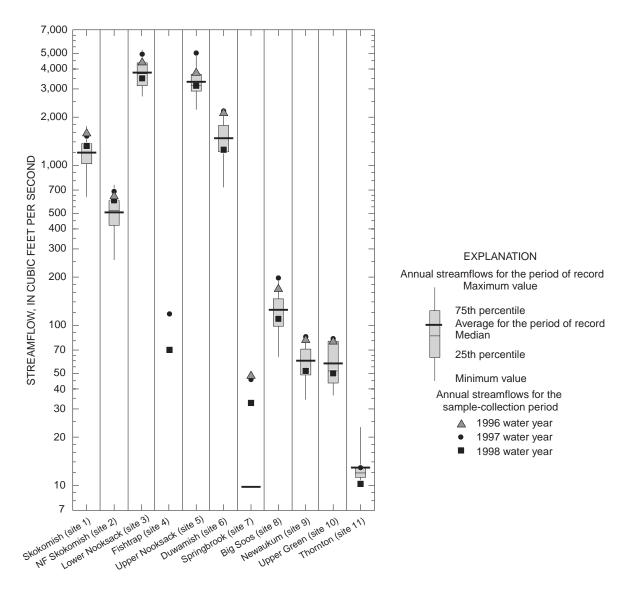


Figure 4. Distribution of annual streamflows for the period of record at fixed sites, and annual streamflows for individual water years of the sample-collection period in the Puget Sound Basin study unit, Washington.

Daily flows in the NF Skokomish, Nooksack, Duwamish, and upper Green Rivers followed seasonal patterns typical of PSB rivers with headwaters in the mountains. These patterns include two periods of high flows—one in fall and winter with the arrival of the rainy season and one during spring snowmelt; and a low-flow period in late summer (August-September). Daily flows in the small lowland streams followed a typical seasonal pattern of one high-flow period during fall and winter, followed by flows tapering off in magnitude during spring and a low-flow period in late summer. Daily flows in the Skokomish at site 1 followed a season pattern like that of the lowland streams, with only one high-flow period during the wet season. This is probably due mostly to flow regulation of the NF Skokomish, which captures much of the snowmelt in reservoirs. In the large rivers, above-average snowpacks during the study helped to contribute to occasional flooding during rain-on-snow events, such as in water years 1996 and 1997, but also helped to sustain summertime flows at normal or above-normal levels.

Water Quality—Chemistry, Standards and Criteria, and Loads

Water in the large rivers (Skokomish, Nooksack, Green-Duwamish), and in two streams in the Lowlands (Big Soos and Newaukum) with large drainage areas relative to other lowland streams in the study, was characterized by dilute water chemistry with dissolvedsolids concentrations less than 130 mg/L; pH values ranging from 6.9 to 8.2 units; and high dissolvedoxygen concentrations with medians ranging from 10.2 to 12.8 mg/L and minimums not less than 7.6 mg/L. Water in the three other streams in the Lowlands (Fishtrap, Springbrook, and Thornton) had dissolvedsolids concentrations as high as 320 mg/L; pH values ranging from 6.9 to 8.7 units; and dissolved oxygen with median concentrations ranging from 5.6 to 10.4 mg/L and minimum concentrations as low as 2.3 mg/L (in Springbrook).

Nutrient concentrations were generally higher in the small streams of the Lowlands than in the large rivers and were also higher during periods of storm runoff. Total nitrogen concentrations (the sum of nitrite, nitrate, ammonia, and organic nitrogen concentrations) averaged from 1.1 to 3.6 mg/L in the small streams of the Lowlands, compared with average concentrations of less than 1.0 mg/L in the large rivers. Average total nitrogen concentrations in the reference and forested rivers were less than 0.1 mg/L. Nutrient loads ranged from 6 ton/yr (tons per year) of total nitrogen in the Green to 3,200 ton/yr of total nitrogen in the lower Nooksack, and from about 2 ton/yr of total phosphorus in the lower Nooksack. Per unit area of drainage basin, however, Fishtrap transported the most nitrogen on an annual basis, 8.8 ton/mi² (tons per square mile). The largest total phosphorus yield, 1.2 ton/mi², was from the upper Nooksack. Inorganic nitrogen and total phosphorus loads calculated for this study were nearly all higher than loads estimated for the period 1980-93 by Embrey and Inkpen (1998) using historical data compiled from Washington State Department of Ecology's and King County's long-term monitoring programs. Suspended-sediment concentrations were highest in the large rivers, with averages ranging from 85 to 443 mg/L. Maximum concentrations of more than 3,200 mg/L were measured in samples from the upper Nooksack (site 5) followed by 1,500 mg/L in a sample from the Skokomish (site 1).

During this study, the relative quality of water among the 11 sites ranged from exceptionally high in the NF Skokomish to fair in Springbrook and Thornton Creeks. Descriptors of the relative quality of water used in this report were based on concentrations of chemicals, dissolved oxygen, and suspended sediment and values of specific conductance and water temperature.

Out of 86 pesticide compounds analyzed, 36 compounds (26 herbicides, one herbicide transformation product, and nine insecticides) were detected in samples from the four sites intensively studied during 1996-98. Those pesticides most frequently detected were the herbicides prometon, simazine, and atrazine and the insecticide diazinon. Most of the detections were in samples from the small lowland streams Thornton and Fishtrap (fig. 5).

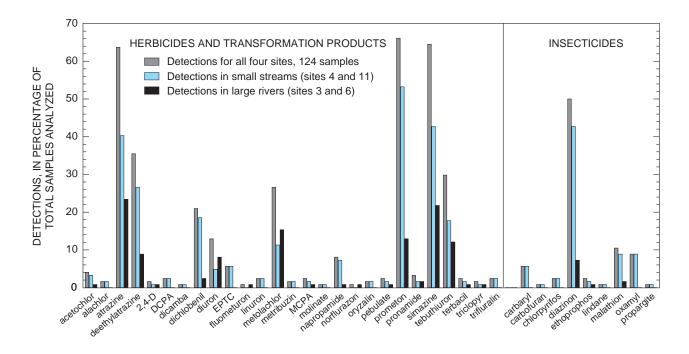


Figure 5. Percentage of detections of pesticides in water samples from the four intensive fixed sites—site 11, Thornton Creek, and site 4, Fishtrap Creek (small streams) and site 6, Duwamish River, and site 3, Iower Nooksack River (large rivers)—in the Puget Sound Basin study unit, Washington.

Eleven VOCs were detected at concentrations above the 1999 LRLs in samples from the four intensively studied sites (fig. 6). Each detected compound belonged to one of three general classes fuel-related compounds, the trihalomethanes, or solvents. Compounds detected most often included methylbenzene and trichloromethane. As with pesticides, more types of VOCs were detected and detection frequencies were higher in the small streams (Thornton and Fishtrap) than in the large rivers (lower Nooksack and Duwamish).

At most sites, existing and applicable standards and criteria for surface-water quality and drinkingwater supplies and freshwater-chronic criteria for the protection of aquatic life (hereafter referred to as aquatic-life criteria) were nearly always met. One measurement at the time of sample collection at each of four sites did not meet Washington State standards (State of Washington, 1992) for dissolved-oxygen concentrations, and one sample at Thornton did not meet the State standard for pH (table 2). Numerous samples exceeded the U.S. Environmental Protection Agency (USEPA) 1996 Secondary Maximum Contaminant Levels (SMCL) for iron and manganese. On many occasions, samples from Springbrook did not meet standards and criteria for temperature and for dissolved-oxygen, iron, and manganese concentrations. Concentrations of nitrate, chloride, fluoride, sulfate, and VOCs in all samples from all 11 sites met aquaticlife criteria and USEPA drinking water Maximum Contaminant Levels (MCL) and SMCLs. Concentrations of four insecticides, however, did not meet aquatic-life criteria in a few samples from Fishtrap and the Duwamish, and in several samples from Thornton.

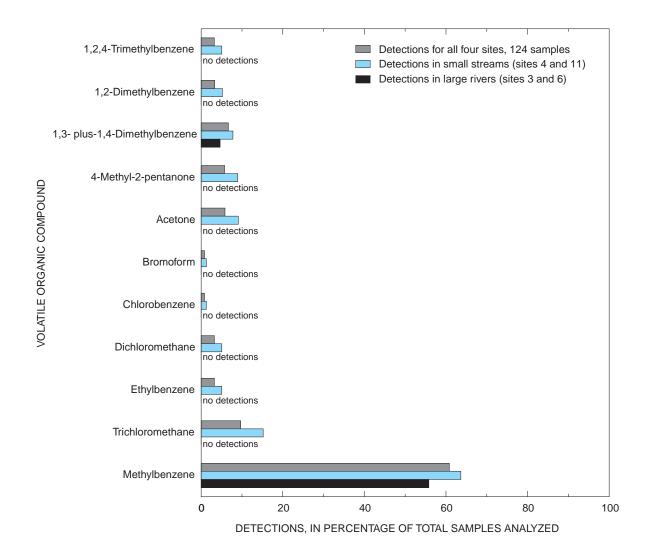


Figure 6. Percentage of detections of VOCs at concentrations above the 1999 laboratory reporting level in samples from four intensive fixed sites—site 11, Thornton Creek, and site 4, Fishtrap Creek (small streams) and site 6, Duwamish River, and site 3, Iower Nooksack River (large rivers)—in the Puget Sound Basin study unit, Washington.

 Table 2.
 Summary of standards and criteria for selected water-quality properties, inorganic constituents, and pesticides, and number of samples that did not meet criteria during the period 1996–98 in the Puget Sound Basin study unit, Washington

[USEPA drinking-water standards and HAL: U.S. Environmental Protection Agency (1996). USEPA Aquatic Life: U.S. Environmental Protection Agency, 1998, CCC (criterion continuous concentration). Because temperature and dissolved oxygen criteria are species dependent and for a warmwatercoldwater matrix, USEPA criteria are not listed. Washington State water-quality standards: State of Washington, 1992. Abbreviations: MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; HAL, health advisory level; USEPA, U.S. Environmental Protection Agency; mg/L, milligrams per liter; µg/L, micrograms per liter: N, nitrogen; –, no value]

Constituent or property	waters	drinking standards	HAL	USEPA Aquatic		gton State lity stand		Number and (percent) of total	
oblishing in property -	MCL	SMCL	IIAE	Life	Class AA	Class A	Class B	samples not meeting criteria	(Washington State Class; number of samples)
Temperature (degrees Celsius)	_	_	_	-	¹ 16.0	¹ 18.0	¹ 21.0	6 (1.5)	Nooksack at Brennan (A;2), Springbrook (A;2), Thornton (A;2)
Dissolved oxygen (mg/L)	_	-	_	-	² 9.5	² 8.0	² 6.5	29 (7.0)	Skokomish (AA;1), Nooksack at North Cedarville (AA;1), Green (AA;1), Springbrook (A;25)
pH (units)	-	6.5 to 8.5	-	6.5 to 9.0	6.5 to 8.5	6.5 to 8.5	6.5 to 8.5	1 (0.2)	Thornton (A;1)
Nitrite (mg/L as N)	1.0	_	_	_	_	_	_	0	_
Nitrite + Nitrate (mg/L as N)	10	-	-	_	_	_	_	0	_
Iron (µg/L)	_	300	-	1,000	_	_	_	48 (11.8)	Skokomish (AA;2), Fishtrap (A;11), Duwamish (B;7), Springbrook (A;25), Newaukum (A;1), Green (AA;1), Thornton (A;1)
Manganese (µg/L)	-	50	-	_	-	_	_	100 (24.5)	Fishtrap (A;43), Duwamish (B;10), Springbrook (A;36), Thornton (A;11)
Chloride (mg/L)	_	250	_	230	-	_	_	0	_
Fluoride (mg/L)	4	2	-	_	-	-	-	0	_
Sulfate (mg/L)	500	250	_	_	_	_	_	0	_
Carbaryl (µg/L)	_	-	700	³ 0.017	-	_	_	5 (4.0)	Fishtrap (A;3), Thornton (A;2)
Chlorpyrifos (µg/L)	_	_	20	.041	_	_	_	1 (.8)	Thornton (A;1)
Diazinon (µg/L)	_	-	0.6	⁴ .04				21 (16.9)	Fishtrap (A;5), Duwamish (B;2), Thornton (A;14)
Lindane $(\mu g/L)^1$	0.2	_	.2	⁵ .01; ⁶ .08	-	_	-	1 (.8)	Thornton (A;1)

¹ Not to exceed due to human activities (when natural conditions exceed value shown, no temperature increases will be allowed that will raise the receiving water temperature by greater than 0.3 degrees Centigrade).

 2 Not to be less than standard shown.

³ Norris and Dost (1992).

⁴ Menconi and Cox (1994).

⁵ International Joint Commission Canada and United States (1977).

⁶ State of Washington (1992)

Skokomish River Basin

The Skokomish River Basin is located entirely within the Olympic Mountains physiographic province. Population density in the basin is low, in the range of 0-50 people per square mile (Staubitz and others, 1997). Two basic fixed sites were established in the basin (fig. 1 and table 1): site 1 on the mainstem Skokomish and site 2 on the NF Skokomish. Because nearly all flow in the NF Skokomish is diverted away from the mainstem through Cushman Powerhouse No. 2 to Hood Canal, site 1 is an indicator of the quality of water mostly from the SF Skokomish and from the lower mainstem Skokomish. Forestry practices dominate in the SF Skokomish River Basin and a small amount of the drainage area of the lower mainstem is used for agriculture. The area drained by site 1 is 227 mi^2 , including 99 mi² in the NF Skokomish River Basin that is noncontributing except during dam spillage. Site 2 is an indicator of reference or background conditions in a forested basin with a drainage area of 57.2 mi².

Skokomish River Basin Hydrology

Annual streamflows during the study period exceeded the mean annual streamflow for the period of record at both site 1 and site 2 (fig. 4). Precipitation in amounts above normal during fall and winter of 1995-96 and storms with heavy rainfall in November 1995, February 1996, and April 1996 contributed to abovenormal streamflows and produced extreme high flows on several days. From March through May, daily streamflows were variable, ranging from well below normal to above normal. Daily streamflows at both sites during late spring 1996 were mostly below the 25th quartile. At site 1, summer and early fall flows were within the 25th and 75th interquartile range (fig. 7), whereas at site 2, flows remained mostly below the 25th quartile (fig. 8).

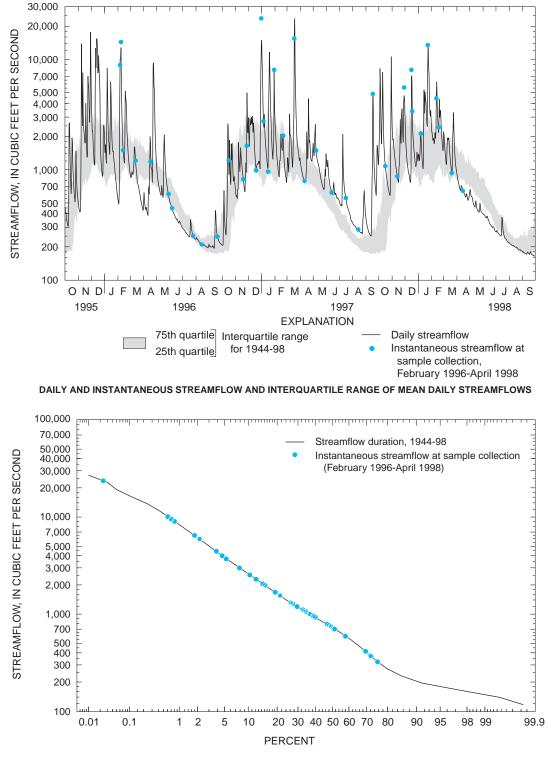
Water year 1997 began with streamflows mostly normal during fall and early winter; however, heavy rainfall at the end of December caused extreme high flows in both rivers. Above-normal precipitation and heavy rainfall contributed to high flows again during parts of January, February, and March. During spring and summer 1997, most all daily flows were near normal or above normal, supported in part by an average to above-average snowpack that year. The water year ended in September with flows well above the 75th quartile.

Daily streamflows continued to be above normal at the start of water year 1998. At the onset of winter, flows were mostly normal, even though precipitation was less than the 25th quartile (fig. 2). In January 1998, in response to increasing precipitation, streamflows rose above the 75th quartile, but by spring, daily flows dropped below normal. At site 1, flows remained below the 25th quartile through the end of the study period in April 1998. At site 2, daily flows were mostly within the interquartile range through the end of the study period.

Streamflow magnitude at the time of sample collection at sites 1 and 2 spanned a wide range, from high flows that are exceeded less than 1 percent of the time to low flows that are exceeded more than 90 percent of the time (figs. 7 and 8). Sample collections were also evenly distributed over the range of flows that can occur at these sites. One sample was collected on March 18 at both sites during the regional storm that produced a peak flow for 1997 at both sites.

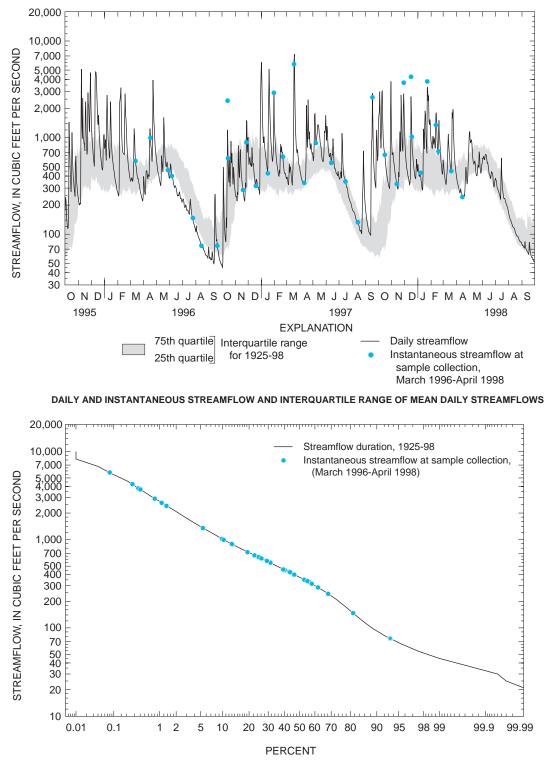
Site 1: Mean annual streamflow for the Skokomish for 55 years of record was 1,200 ft³/s, which was exceeded by annual streamflows of 1,580, 1,500, and 1,320 ft³/s for water years 1996-98, respectively. In water year 1997, heavy rainfall on December 30, 31, and January 1 brought the river to a daily mean of 15,000 ft³/s and over flood stage. One sample was collected during this storm when the highest instantaneous flow at this site for the study period was measured (fig. 7). The flow on March 19, 1997, estimated to be 23,500 ft³/s, approached the highest recorded daily flow of 30,000 ft³/s for this site.

Site 2: Mean annual streamflow for the NF Skokomish for 74 years of record was 508 ft³/s, which was exceeded by annual streamflows of 639, 677, and 604 ft³/s for water years 1996-98, respectively. In water year 1997, the rainstorms at the end of December and on New Years Day 1997 produced an annual peak flow of 8,140 ft³/s at this site. The March 18–20 rainstorm resulted in a daily flow on March 19, 1997, of 7,300 ft³/s, which is exceeded less than 0.02 percent of the time.



PERCENTAGE OF TIME STREAMFLOWS ARE EQUALED OR EXCEEDED AND INSTANTANEOUS STREAMFLOW

Figure 7. Daily and instantaneous streamflow at the time of sample collection, interquartile range of mean daily streamflows for the period of record, and percentage of time streamflows are equaled or exceeded at the Skokomish River in the Puget Sound Basin study unit, Washington.



PERCENTAGE OF TIME STREAMFLOWS ARE EQUALED OR EXCEEDED AND INSTANTANEOUS STREAMFLOW

Figure 8. Daily and instantaneous streamflow at the time of sample collection, interquartile range of mean daily streamflows for the period of record, and percentage of time streamflows are equaled or exceeded at the North Fork Skokomish River (site 2) in the Puget Sound Basin study unit, Washington.

Skokomish River Basin Water Quality

A total of 37 water samples from site 1 and 33 samples from site 2 were analyzed for physical properties, field parameters, and concentrations of inorganic constituents, organic carbon, and suspended sediment. Water in both rivers was chemically dilute, as indicated by the conductivity and dissolved-solids concentrations. In samples from site 1, conductivity ranged from 30 to 80 μ S/cm with a median of 58 µS/cm, and dissolved-solids concentrations ranged from 25 to 64 mg/L with a median of 41 mg/L (table 3). In samples from site 2, conductivity ranged from 34 to 100 μ S/cm with a median of 74 μ S/cm, and dissolved-solids concentrations ranged from 21 to 67 mg/L with a median of 45 mg/L (table 4). On the basis of median concentrations, the dominant cation and anion making up the dissolved solids were calcium and bicarbonate, respectively (fig. 9). Concentrations of nutrients were low, with at least one-half of the values for organic nitrogen and phosphorus below laboratory MRLs (tables 3 and 4). However, at site 1, about 10 percent of the total phosphorus concentrations were greater than 0.1 mg/L, USEPA's (1986a) desired goal to prevent nuisance plant growth in streams. With only a few exceptions, applicable standards and criteria for drinking water, ambient water quality for beneficial uses, and the protection of aquatic life were met by the water quality at both sites.

In addition to monthly routine samples, 11 of the 37 samples targeted streamflows during rainstorms or snowmelt events. Maximum concentrations of total nitrogen, total phosphorus, and suspended sediment were typically in samples collected on the rising limb or near the peak of the hydrograph during these runoff events, such as occurred in March and December 1997 and in January 1998 (figs. 10 and 11). Concentrations of total phosphorus, dissolved and suspended organic carbon, iron, and suspended sediment tended to vary directly with streamflows, as indicated by Kendall's tau (τ) , which ranged from 0.3 to 0.7 (<u>table 5</u>). The positive correlations are indicative of the tendency for particulate matter and constituents adsorbed to the particles to enter streams in storm runoff and to be resuspended from the stream channel with rising water levels and stream energy. Concentrations of dissolved solids and major ions, such as bicarbonate, varied inversely with streamflows ($\tau = -0.6$ to -0.9), which generally indicates dilution effects from rain or snowmelt.

Seasonality in water quality is defined by the long-term hydrographs for these sites (figs. 7 and 8). In the Skokomish River Basin, the high-flow period is typically from October through January. The transition period, from February through June (at site 1) or through July (at site 2), is a time of generally lower streamflows than in winter and diminishing flows with summer's approach. The low-flow period is from July through September at site 1 and from August through September at site 2. The highest concentrations of total nitrogen, total phosphorus, and suspended sediment tended to occur during the high-flow period (figs. 10 and 11). The one time that an instantaneous dissolvedoxygen concentration did not meet the State's minimum standard was in summer (July 1996).

Site 1: The water in the Skokomish was of generally high quality except at times when suspendedsediment concentrations were large. Ten percent of the samples had suspended-sediment concentrations greater than 600 mg/L with a maximum of 1,470 mg/L observed on December 16, 1997. On one occasion, the concentration of dissolved oxygen measured at the time of sample collection was 9.3 mg/L and did not meet the Washington State standard of 9.5 mg/L minimum concentration for a Class AA water body (see table 2). On two occasions, iron concentrations of as much as 430 µg/L exceeded the USEPA SMCL of 300 µg/L for drinking water. Nitrate, with a median concentration of 0.09 mg/L, and total organic nitrogen, with a median of 0.08 mg/L (estimated by log-probability regression, Helsel and Cohn, 1988), were the dominant nitrogen species (fig. 9). Median concentrations of nutrients, suspended sediment, and dissolved and suspended organic carbon in samples from site 1 were generally greater than those from site 2(fig. 9).

Site 2: The water in the NF Skokomish was of exceptionally high quality. Suspended sediment and iron concentrations in samples were low, with iron concentrations equal to or less than 25 μ g/L and 90 percent of suspended sediment concentrations less than 46 mg/L (table 4). The maximum suspendedsediment concentration observed during the study was 122 mg/L. As at site 1, nitrate, with a median concentration of 0.05 mg/L, and total organic nitrogen, with a median of 0.04 mg/L (estimated by logprobability regression), were the dominant nitrogen species (fig. 9). In the low-flow period at this site, many of the phosphorus and orthophosphate concentrations were below laboratory MRLs. **Table 3**. Summary of values of field measurements and concentrations of nutrients, major ions, organic carbon, and suspended sediment in samples from the Skokomish River (site 1) in the Puget Sound Basin study unit, Washington

[Measurement or concentration - Percentile: Percentiles for data sets with 10 percent or more censored data (values less than the MRL) are estimated by log-probability regression (Helsel and Cohn, 1988). Concentrations are dissolved and in milligrams per liter unless otherwise specified. Abbreviations: MRL, minimum reporting level; µS/cm, microsiemens per centimeter at 25 degrees Celsius; CaCO₃, calcium carbonate; <, less than; µg/L, micrograms per liter]

				Measur	ement or co	ncentratio	n		
-				Percentile					Number of
Constituent or property	Mini- mum	10	25	50 (Median)	75	90	Maxi- mum	Number of samples	samples below MRL (see t <u>ables</u> <u>A1-A3</u>)
Water temperature (degrees Celsius)	5.4	5.5	6.1	7	10.2	12.6	14.6	37	0
Specific electrical conductance, $(\mu S/cm)$	30	37	47	58	67	78	80	37	0
pH (units)	7.0	7.2	7.3	7.5	7.6	7.7	7.9	37	0
Dissolved oxygen	9.3	9.9	10.6	11.6	12	12.3	12.5	36	0
Ammonia nitrogen	< 0.015	< 0.015	< 0.015	0.013	0.02	0.03	0.04	37	25
Ammonia-plus-organic nitrogen	<.1	<.1	<.1	<.1	<.1	<.1	.2	37	36
Ammonia-plus-organic nitrogen, total	<.1	<.1	<.1	.08	.14	.24	.45	37	34
Nitrite nitrogen	<.01	<.01	<.01	<.01	.01	.01	.02	37	30
Nitrite-plus-nitrate nitrogen	<.05	.05	.06	.09	.11	.14	.15	37	5
Phosphorus, total	<.01	<.01	<.01	.02	.06	.25	.57	37	15
Phosphorus	<.01	<.01	<.01	<.01	<.01	<.01	.14	37	31
Orthophosphate phosphorus	<.01	<.01	<.01	.01	.012	.02	.05	37	18
Alkalinity (as CaCO ₃)	14	16	22	27	30	35	41	37	0
Bicarbonate (as CaCO ₃)	18	19	27	33	38	43	50	37	0
Calcium	3.5	4.3	5.6	7.2	8.1	8.8	9.5	37	0
Magnesium	.81	1.0	1.3	1.7	1.9	2.4	2.5	37	0
Sodium	1.1	1.3	1.5	1.8	2.1	2.2	2.3	37	0
Potassium	<.1	<.1	<.1	<.1	.11	.13	.3	37	19
Chloride	.6	.88	1.1	1.3	1.4	1.5	1.8	37	0
Sulfate	.59	.69	.9	1.2	1.3	1.5	2.5	37	0
Fluoride	<.1	<.1	<.1	<.1	<.1	<.1	<.1	37	37
Silica	6.2	7.8	9.4	11	12	14	14	37	0
Iron, in μg/L	<3.0	4.1	6.9	12	45.5	81	430	37	5
Manganese, in µg/L	<4.0	2.8	2.9	3	5	7	11	37	4
Dissolved solids, residue at 180 degrees Celsius	25	26	32.5	41	47.5	54	64	37	0
Organic carbon	.2	.3	.4	.7	1.1	1.4	2.5	36	0
Organic carbon, suspended	<.10	<.10	.1	.2	.9	2.2	6.8	37	7
Sediment, suspended	<1	1	2	25.5	261	619	1,470	34	0

Table 4. Summary of values of field measurements and concentrations of nutrients, major ions, organic carbon, and suspended sediment in samples from the North Fork Skokomish River (site 2) in the Puget Sound Basin study unit, Washington

[Measurement or concentration - Percentile: Percentiles for data sets with 10 percent or more censored data (values less than the MRL) are estimated by log-probability regression (Helsel and Cohn, 1988). Concentrations are dissolved and in milligrams per liter unless otherwise specified. Abbreviations: MRL, minimum reporting level; µS/cm, microsiemens per centimeter at 25 degrees Celsius; CaCO₃, calcium carbonate; <, less than; µg/L, micrograms per liter]

				Measure	ment or co	ncentratio	1		
				Percentile					Number of
Constituent or property	Mini- mum	10	25	50 (Median)	75	90	Maxi- mum	Number of samples	samples below MRL (see <u>tables</u> <u>A1-A3</u>)
Water temperature (degrees Celsius)	3.3	3.5	4.2	5	7.8	11.0	12.5	33	0
Specific electrical conductance, (µS/cm)	34	40	60	74	83.5	91	100	33	0
pH (units)	7.2	7.4	7.5	7.7	7.8	7.9	7.9	33	0
Dissolved oxygen	10.2	11.1	11.8	12.8	13.3	13.8	14.9	33	0
Ammonia nitrogen	< 0.01	< 0.015	< 0.015	0.014	0.02	0.03	0.04	33	23
Ammonia-plus-organic nitrogen	<.1	<.1	<.1	<.1	<.1	<.1	<.1	33	33
Ammonia-plus-organic nitrogen, total	<.1	<.1	<.1	.04	.07	.12	.23	33	30
Nitrite nitrogen	<.01	<.01	<.01	<.01	<.01	<.01	.01	33	28
Nitrite-plus-nitrate nitrogen	<.05	.025	.035	.05	.09	.1	.147	33	17
Phosphorus, total	<.01	<.01	<.01	<.01	.01	.05	.08	33	24
Phosphorus	<.01	<.01	<.01	<.01	<.01	.009	.015	33	30
Orthophosphate phosphorus	<.01	<.01	<.01	<.01	.01	.014	.02	33	24
Alkalinity (as CaCO ₃)	14	16	24.5	29	33.5	37	40	33	0
Bicarbonate (as CaCO ₃)	17	19	29.5	36	40.5	45	49	33	0
Calcium	4.9	6.3	9.2	11	13	14	16	33	0
Magnesium	.4	.5	.7	.82	1.0	1.1	1.1	33	0
Sodium	.7	.9	1.15	1.4	1.6	1.75	1.9	33	0
Potassium	<.1	.1	.1	.12	.15	.2	.2	33	3
Chloride	.43	.49	.52	.6	.74	.88	.92	33	0
Sulfate	1.8	1.9	3.8	4.6	5.7	6.0	7.4	33	0
Fluoride	<.1	<.1	<.1	<.1	<.1	<.1	<.1	33	33
Silica	2.6	3.3	4.1	5.2	5.6	5.8	5.9	33	0
Iron, in µg/L	<3.0	<3.0	<3.0	3.5	9.5	17	25	33	21
Manganese, in µg/L	<1	<1	<1	<1	<1	1	2	33	29
Dissolved solids, residue at 180 degrees Celsius	21	27	37.5	45	50	55	67	33	0
Organic carbon	.4	.4	.6	.6	1.45	2.2	3.7	33	0
Organic carbon, suspended	<.1	<.1	<.1	.1	.2	1.2	1.6	31	12
Sediment, suspended	<1	<1	<1	1	6	46	122	33	9

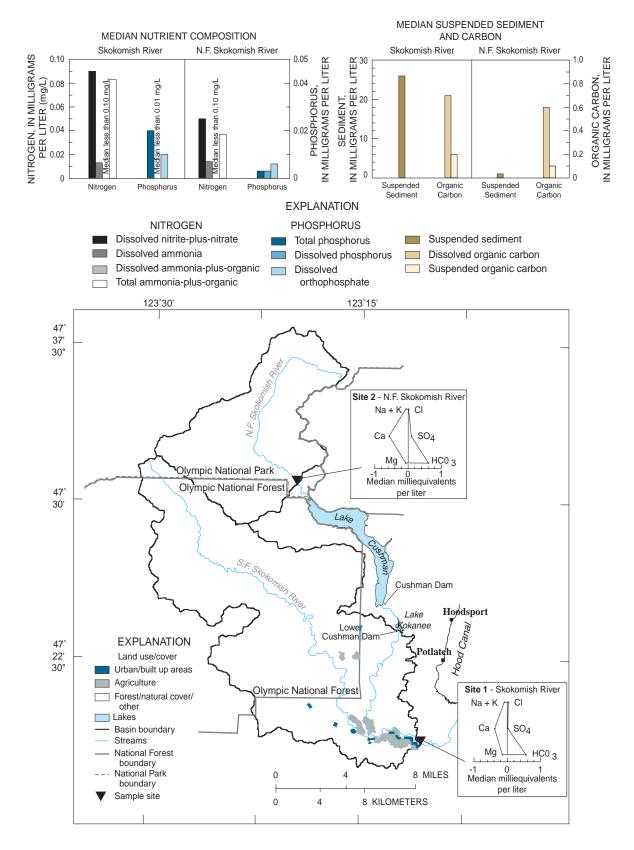


Figure 9. Median concentrations of nutrients, suspended sediment, organic carbon, and major ions in samples from the Skokomish River (site 1) and the North Fork Skokomish River (site 2) in the Puget Sound Basin study unit, Washington.

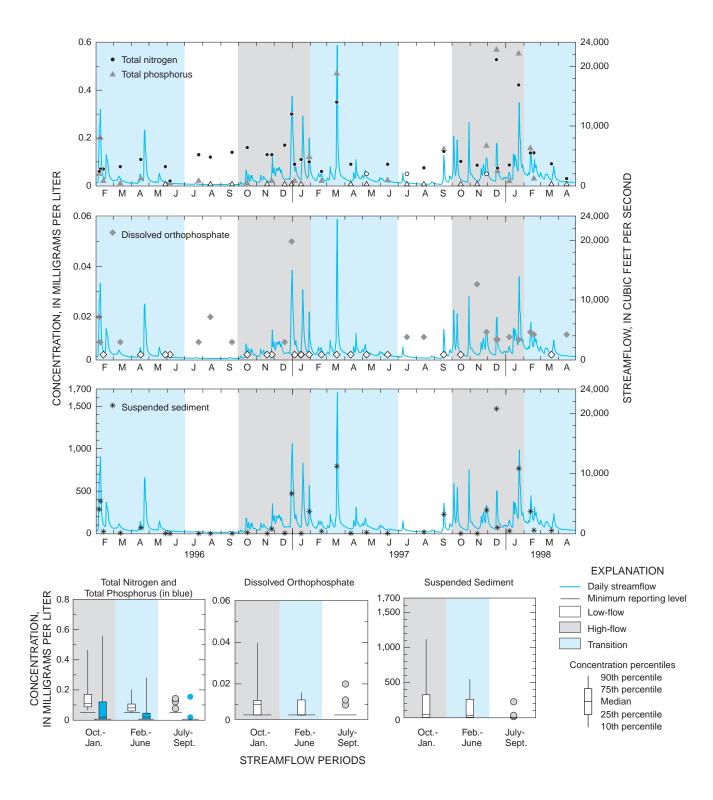


Figure 10. Time series of streamflow and concentrations of total nitrogen, total phosphorus, dissolved orthophosphate phosphorus, and suspended sediment in samples, and concentrations by three streamflow periods, for the Skokomish River (site 1) in the Puget Sound Basin study unit, Washington. (Truncated boxplots of concentration percentiles require a minimum of nine observations, otherwise concentrations are plotted as individual points. Censored data in the time-series graphs are shown as an open symbol. Boxplots are truncated at the minimum reporting level indicated by solid line.)

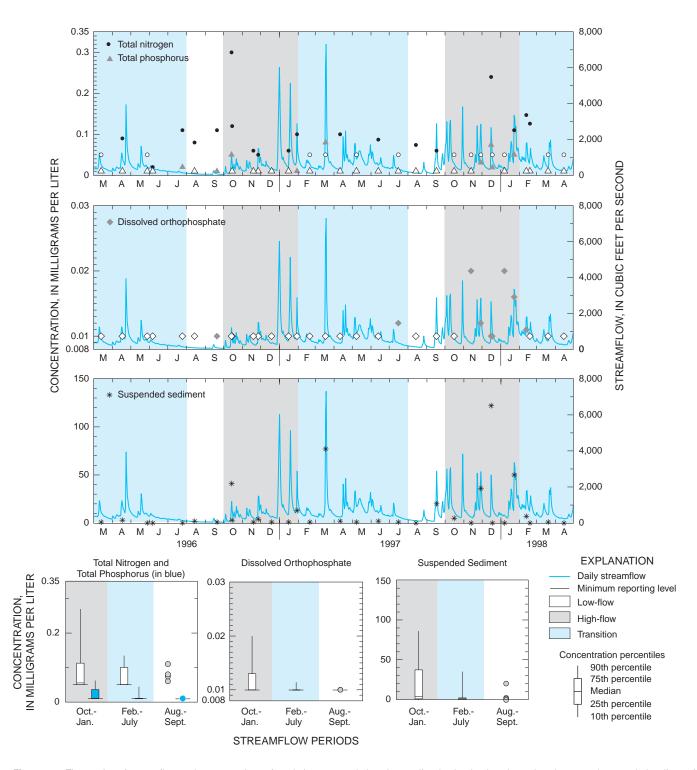


Figure 11. Time series of streamflow and concentrations of total nitrogen, total phosphorus, dissolved orthophosphate phosphorus, and suspended sediment in samples, and concentrations by three streamflow periods, for the North Fork Skokomish River (site 2) in the Puget Sound Basin study unit, Washington. (Truncated boxplots of concentration percentiles require a minimum of nine observations, otherwise concentrations are plotted as individual points. Censored data in the time-series graphs are shown as an open symbol. Boxplots are truncated at the minimum reporting level indicated by solid line.)

Table 5.Correlation between selected water-quality characteristics or concentrations of chemicalconstituents and streamflow for the Skokomish River (site 1) and the North Fork Skokomish River (site 2) inthe Puget Sound Basin study unit, Washington

W-4	Kendall's tau corre	elation coefficient
Water-quality characteristic or chemical constituent	Skokomish River (Site 1)	North Fork Skokomish River (Site 2)
Specific electrical conductance	-0.87	-0.86
Dissolved solids	73	65
Total nitrogen	.15	.03
Dissolved nitrite-plus-nitrate nitrogen	.02	02
Total ammonia-plus-organic nitrogen	.05	.09
Dissolved ammonia-plus-organic nitrogen	09	13
Total phosphorus	.54	.27
Dissolved orthophosphate phosphorus	.08	.08
Dissolved organic carbon	.52	.59
Suspended organic carbon	.71	.49
Suspended sediment	.74	.52
Bicarbonate	80	87
Iron	.41	.48
Manganese	.23	.21

Nooksack River Basin

The Nooksack River originates within the Cascade Range physiographic province. Below the confluence of the three forks, the river drains the Puget Sound Lowlands province. Population density in the basin is low, with 0-50 people per square mile and some population centers of 51-250 people per square mile (Staubitz and others, 1997). Three basic fixed sites are in the Nooksack River Basin (fig. 1 and table 1): site 3 on the lower mainstem Nooksack; site 4 on Fishtrap Creek, and site 5 on the upper mainstem Nooksack. Site 3 is an integrator of the quality of water from the Nooksack River Basin, which consists of high-altitude mountains with glacier and snowfields, forests, a few small population centers along the lower mainstem, and intensive agricultural practices in the Lowlands. The river drains an area of 790 mi^2 at site 3. Site 4 is an indicator of intense agricultural practices (dairy, berries, potatoes, corn, poultry); however, urban/suburban development in parts of the basin (Canada and the nearby city of Lynden) also contributes to the water-quality characteristics. Fishtrap Creek at site 4 drains an area of 38.1 mi². Site 5 is an indicator of water quality from forest practices and from undisturbed high-mountain lands of the upper Nooksack River Basin. The Nooksack River at site 5 drains an area of 589 mi².

Nooksack River Basin Hydrology

Water year 1996 and 1997 annual streamflows were greater than the mean annual streamflow for the period of record at site 3 and site 5 (fig. 4). Annual flow for 1998 was about equal to the mean annual flow at these two sites. No long-term record existed at site 4 for comparing annual or daily flows observed during the study. Flow variability at site 4 as it related to climate during the sampling period is illustrated by the daily-streamflow hydrograph recorded during this study. Precipitation recorded at Bellingham in amounts above normal during fall and winter of 1995-96 contributed to above-normal streamflows. In addition, storms with heavy rainfall from November 1995 through April 1996 produced extreme high flows at times (figs. 12, 13, and 14). Daily streamflows in March were near normal, but from April through May flows ranged from well above normal to below normal. In summer and early fall, flows were generally within the 25th and 75th interquartile range except for a few

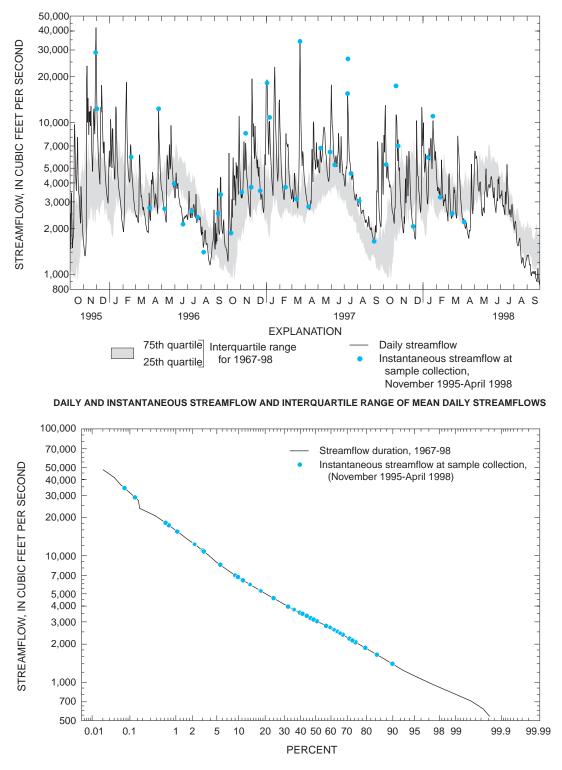
days in mid-September when locally heavy rainstorms brought the flows to above normal. During the dry season, above-normal snowpack and glacial meltwater helped to sustain flows in the mainstem Nooksack River.

In water year 1997, streamflows were mostly near the upper quartile of historical flows, with abovenormal precipitation contributing to extreme high flows at times from November through March. The regional storm of March 18–20, 1997, generated extreme high flows at all three sites. Near the end of summer, the wet season arrived early, with above-normal rainfall raising September flows to above the 75th quartile.

Daily streamflows continued to be above normal at the start of water year 1998, with October precipitation 140 percent of normal (see fig. 3). During winter 1997–98, below-normal precipitation kept November, December, and February flows mostly within the interquartile range. With more moderate rainfall amounts in spring of 1998, daily flows were mostly normal until April, the end of the study period. Precipitation only 40 percent of normal resulted in low flows during April 1998.

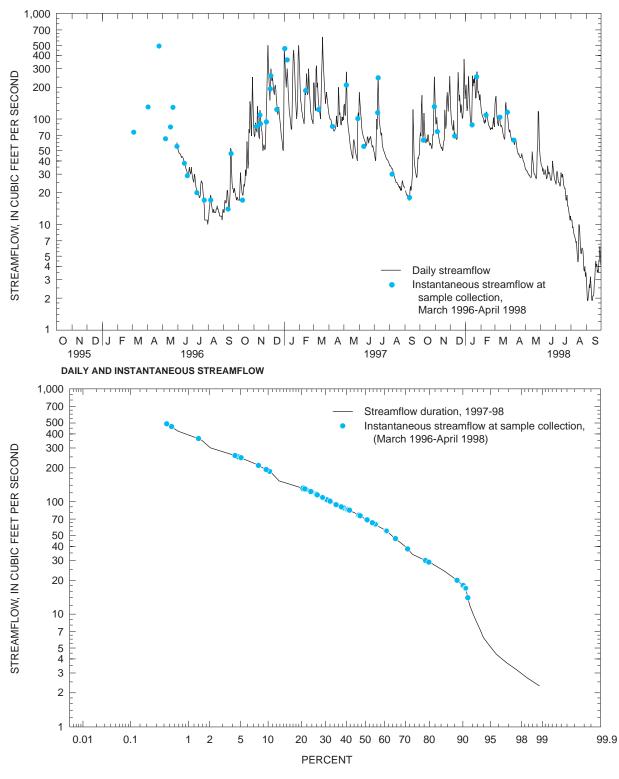
Magnitude of streamflows at the time of sample collection at sites 3 and 5 spanned a wide range, from high flows that are exceeded less than 1 percent of the time to low flows that are exceeded more than 90 percent of the time (figs. 12 and 14). Sample collections were relatively evenly distributed over the range of flows that can occur at these sites, with some clustering of samples between the 50th and 80th percentiles at site 5 (fig. 14). Water samples were collected at sites 3 and 5 during the November 1995 storm that generated the highest daily flow observed at these two sites during the 3-year study period. Samples were also collected at both sites on March 20, 1997, during the regional storm that produced a peak flow for 1997 at each site.

Site 3: Mean annual streamflow for the lower Nooksack for 32 years of record at the gage upstream (12213100, Nooksack River at Ferndale) was 3,800 ft³/s, which was exceeded by annual flows of 4,390 and 5,270 ft³/s during 1996 and 1997, respectively. Annual streamflow for water year 1998 was 3,500 ft³/s. The March 1997 regional storm produced a daily mean flow of 33,700 ft³/s, the second highest daily flow observed at this site during the study period.



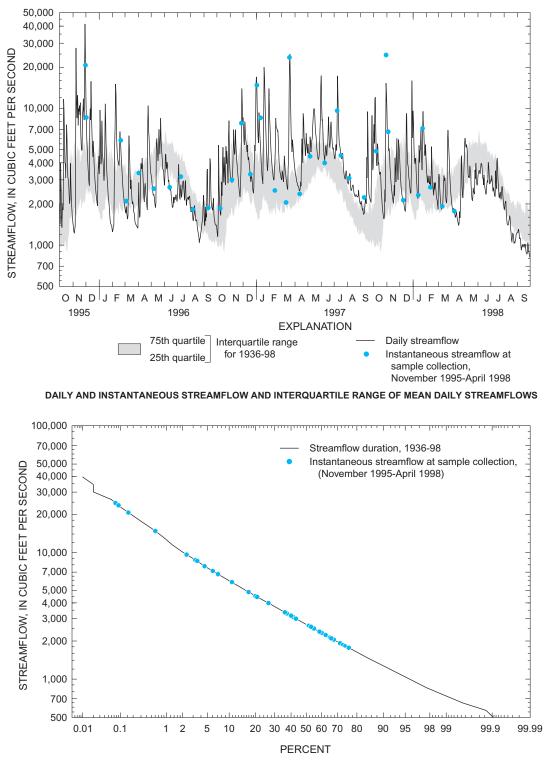
PERCENTAGE OF TIME STREAMFLOWS ARE EQUALED OR EXCEEDED AND INSTANTANEOUS STREAMFLOW

Figure 12. Daily and instantaneous streamflow at the time of sample collection, interquartile range of mean daily streamflows for the period of record, and percentage of time streamflows are equaled or exceeded at the lower Nooksack River (site 3) in the Puget Sound Basin study unit, Washington.



PERCENTAGE OF TIME STREAMFLOWS ARE EQUALED OR EXCEEDED AND INSTANTANEOUS STREAMFLOW

Figure 13. Daily and instantaneous streamflow at the time of sample collection, and percentage of time streamflows are equaled or exceeded and instantaneous streamflow at Fishtrap Creek (site 4) in the Puget Sound Basin study unit, Washington.



PERCENTAGE OF TIME STREAMFLOWS ARE EQUALED OR EXCEEDED AND INSTANTANEOUS STREAMFLOW

Figure 14. Daily and instantaneous streamflow at the time of sample collection, interquartile range of mean daily streamflows for the period of record, and percentage of time streamflows are equaled or exceeded at the upper Nooksack River (site 5) in the Puget Sound Basin study unit, Washington.

Site 4: The average streamflow for Fishtrap for 29 months of record was 78 ft³/s. For the first 4 months of the study period with continuous gage record (June–September 1996), the average flow was 23 ft³/s. Annual flows for water years 1997 and 1998 were 109 and 70 ft³/s, respectively. In water year 1996, late April rainstorms generated high flows from April 23–27, 1996. The storm sample on April 24, 1996, was collected when the highest instantaneous flow (490 ft³/s) for the study period was measured. The March 1997 regional storm produced the highest daily flow, 600 ft³/s, observed during the study period.

Site 5: Mean annual streamflow for the upper Nooksack for 56 years of record at the gage upstream (12210500, Nooksack River at Deming) was 3,320 ft³/s, which was exceeded by annual streamflows of 3,780 and 4,960 ft³/s during 1996 and 1997, respectively. Annual flow for water year 1998 was 3,140 ft³/s. The November 1995 storm resulted in a flow of 41,500 ft³/s on November 29, 1995, the highest recorded daily mean flow for the period of record at this site. The rainstorm of March 1997 produced the second highest daily flow, 25,000 ft³/s, observed at this site during the study period.

Nooksack River Basin Water Quality

Forty-one water samples from site 3 (table 6), 44 samples from site 4 (table 7), and 34 samples from site 5 (table 8) were collected for the analysis of physical properties, field parameters, and concentrations of inorganic constituents, organic carbon, and suspended sediment. Twenty-two samples at site 3 and 32 samples at site 4 were collected for pesticide and VOC analyses. Water quality at the large river sites, sites 3 and 5, met all applicable standards and criteria for drinking water, ambient water quality for beneficial uses, and the protection of aquatic life. However, in several samples from the small stream (site 4), iron and manganese concentrations exceeded USEPA drinking-water SMCLs, and in a few samples, insecticide concentrations exceeded aquatic-life criteria.

High-quality water from the mountain headwaters was an important influence on the water chemistry of the mainstem Nooksack River and contributed to the dilute water chemistry observed in samples from sites 3 and 5. At times, however, large volumes of runoff led to high flows and to flood conditions, in which large amounts of sediment and occasionally high concentrations of total phosphorus were transported. The chemically dilute water chemistry of the Nooksack River was indicated by the conductivity and dissolved-solids concentrations. In addition, as the river flows from site 5 on the upper Nooksack downstream to site 3, these water-quality variables changed very little, as indicated by their median values. For site 3, the median conductivity was 89 μ S/cm (table 6), and for site 5, the median was 75 µS/cm (table 8). Median dissolved-solids concentrations at site 3 was 58 mg/L and at site 5, 49 mg/L. On the basis of median concentrations, the dominant cation and anion making up the dissolved solids in the Nooksack were calcium and bicarbonate, respectively, but in Fishtrap Creek the dissolved solids were composed primarily of calcium, bicarbonate, and sulfate (fig. 15).

Concentrations of nutrients were moderately low in the lower Nooksack, with at least 10 percent of the organic-nitrogen and phosphorus concentrations below laboratory MRLs (<u>table 6</u>); concentrations were low in the upper Nooksack, with at least half of the organic nitrogen and phosphorus concentrations below MRLs (<u>table 8</u>). However, concentrations of total phosphorus in 25 percent of the samples were greater than 0.1 mg/L, USEPA's (1986a) desired goal to prevent nuisance plant growth in streams.

In Fishtrap (site 4), the water chemistry was more concentrated and there were more detections of pesticides and VOCs than in the Nooksack. The water was moderately high in concentrations of inorganic compounds as indicated by a median conductivity of 240μ S/cm and by a median dissolved-solids concentration of 151 mg/L (table 7). Water in Fishtrap was also richer in nutrients than water in the lower or upper Nooksack, with at least 90 percent of the nutrient concentrations (except phosphorus and orthophosphate) above laboratory MRLs. Twenty-five percent of the total phosphorus concentrations were greater than 0.1 mg/L. Ground-water discharge and agricultural and urban land-use activities are likely sources of chemical constituents contributing to the more concentrated water chemistry at site 4.

 Table 6.
 Summary of values of field measurements and concentrations of nutrients, major ions, organic carbon, and suspended sediment in samples from the lower Nooksack River (site 3) in the Puget Sound Basin study unit, Washington

[Measurement or concentration - Percentile: Percentiles for data sets with 10 percent or more censored data (values less than the MRL) are estimated by log-probability regression (Helsel and Cohn, 1988). Concentrations are dissolved and in milligrams per liter unless otherwise specified. Abbreviations: MRL, minimum reporting level; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; CaCO₃, calcium carbonate; <, less than; μ g/L, micrograms per liter]

	Measurement or concentration										
Constituent or property				Percentile					Number of		
constituent of property	Mini- – mum	10	25	50 (Median)	75	90	Maxi- mum	Number of samples	samples below MRL (see <u>tables A1-A3</u>)		
Water temperature (degrees Celsius)	0	4.06	5.55	8.3	11.0	15.8	18	41	0		
Specific electrical conductance (µS/cm)	44	56	73.5	89	116	125	132	41	0		
pH (units)	6.9	7.4	7.5	7.6	7.7	7.8	7.9	41	0		
Dissolved oxygen	8.8	9.7	10.65	11.15	11.9	12.7	13.8	40	0		
Ammonia nitrogen	< 0.015	< 0.015	0.017	0.03	0.045	0.068	0.08	41	12		
Ammonia-plus-organic nitrogen	<.1	.021	.034	.059	.108	.191	.32	41	34		
Ammonia-plus-organic nitrogen, total	<.1	.021	.05	.13	.27	.68	2.4	41	22		
Nitrite nitrogen	<.01	<.01	<.01	.006	.01	.019	.03	41	27		
Nitrite-plus-nitrate nitrogen	.128	.16	.23	.35	.58	.75	.94	41	0		
Phosphorus, total	<.01	<.01	.016	.04	.17	.43	7.3	41	4		
Phosphorus	<.01	<.01	<.01	<.01	.007	.019	.03	41	32		
Orthophosphate phosphorus	<.01	<.01	<.01	.008	.01	.02	.02	41	22		
Alkalinity (as CaCO ₃)	16	18	24.5	30	38.5	42	44	41	0		
Bicarbonate (as CaCO ₃)	19	22	29.5	36	46.5	51	53	41	0		
Calcium	4.7	5.4	7.4	9.5	12	13	14	40	0		
Magnesium	1.4	1.9	2.4	3.0	3.8	4.4	4.6	40	0		
Sodium	.89	1.2	1.9	2.1	3.4	3.7	4.1	40	0		
Potassium	.2	.5	.5	.7	.9	1.1	1.3	40	0		
Chloride	.44	.9	1.4	2.0	3.4	3.8	4.0	40	0		
Sulfate	2.4	3.1	5.9	8.6	11	12	13	40	0		
Fluoride	<.1	<.1	<.1	<.1	<.1	<.1	<.1	40	39		
Silica	3.8	5.5	6.7	8.1	9.6	10	11	40	0		
Iron, in µg/L	6	20	42	66	88	127	190	40	0		
Manganese, in µg/L	4	4.8	6.2	11	16	21	26	40	0		
Dissolved solids, residue at 180 degrees Celsius	31	36.5	50	57.5	76	82	98	40	0		
Organic carbon	.7	.9	1.5	2.2	3.3	4.6	6.8	40	0		
Organic carbon, suspended	<.2	.2	.3	.55	1.3	3.9	12	40	1		
Sediment, suspended	8	15	37	70	301	1,460	2,890	39	0		

Table 7. Summary of values of field measurements and concentrations of nutrients, major ions, organic carbon, and suspended sediment in samples from Fishtrap Creek (site 4) in the Puget Sound Basin study unit, Washington

[Measurement or concentration - Percentile: Percentiles for data sets with 10 percent or more censored data (values less than the MRL) are estimated by log-probability regression (Helsel and Cohn, 1988). Concentrations are dissolved and in milligrams per liter unless otherwise specified. Abbreviations: MRL, minimum reporting level; µS/cm, microsiemens per centimeter at 25 degrees Celsius; CaCO₃, calcium carbonate; <, less than; µg/L, micrograms per liter]

	Measurement or concentration										
				Percentile					Number of		
Constituent or property	Mini- mum	10	25	50 (Median)	75	90	Maxi- mum	Number of samples	samples below MRL (see <u>tables A1-</u> <u>A3</u>)		
Water temperature (degrees Celsius)	2	4.5	6.8	10.2	12.95	15.75	17.4	44	0		
Specific electrical conductance, (µS/cm)	158	179	211	240	255	264	297	44	0		
pH (units)	7.0	7.2	7.4	7.55	7.7	7.7	7.9	44	0		
Dissolved oxygen	8.2	9.1	9.7	10.4	11.1	11.8	12.4	44	0		
Ammonia nitrogen	< 0.015	0.02	0.04	0.09	0.22	0.34	1.2	44	1		
Ammonia-plus-organic nitrogen	<.2	.14	.2	.4	.62	.925	1.8	44	7		
Ammonia-plus-organic nitrogen, total	<.2	.23	.3	.52	.89	1.4	2.9	44	1		
Nitrite nitrogen	<.01	.01	.019	.02	.03	.04	0.07	44	2		
Nitrite-plus-nitrate nitrogen	1.1	2.0	2.3	2.8	3.3	3.9	4.3	44	0		
Phosphorus, total	<.01	.01	.02	.06	.12	.22	.43	44	3		
Phosphorus	<.01	<.01	<.01	.008	.025	.05	.15	44	24		
Orthophosphate phosphorus	<.01	<.01	<.01	.01	.02	.04	.14	44	18		
Alkalinity (as CaCO ₃)	25	35.5	43	49	57	61	63	44	0		
Bicarbonate (as CaCO ₃)	31	43.5	52	60	69.5	74	77	44	0		
Calcium	13	17	20	24	26	27.5	29	44	0		
Magnesium	3.3	4.5	5.5	6.6	7.2	7.6	7.7	44	0		
Sodium	4.3	5.65	6.9	8.1	8.8	9.2	18	44	0		
Potassium	1.8	2.05	2.4	3.0	4.1	4.8	5.5	44	0		
Chloride	5.5	7.8	9.5	10	11	12	28	44	0		
Sulfate	16	22	27	33	36	37.5	42	44	0		
Fluoride	<.1	<.1	<.1	<.1	<.1	<.1	<.1	44	44		
Silica	8	11	13	15	16	17	18	44	0		
Iron, in µg/L	56	100	157	220	319	401	440	44	0		
Manganese, in µg/L	49	73	92	128	160	200	232	44	0		
Dissolved solids, residue at 180 degrees Celsius	104	116	136	151	161	174	195	44	0		
Organic carbon	1.9	2.25	2.8	3.7	5.0	6.7	11	44	0		
Organic carbon, suspended	.2	.4	.5	.95	1.7	2.6	3.9	44	0		
Sediment, suspended	4	6	11	21	42	135	285	42	0		

 Table 8.
 Summary of values of field measurements and concentrations of nutrients, major ions, organic carbon, and suspended sediment in samples from the upper Nooksack River (site 5) in the Puget Sound Basin study unit, Washington

[Measurement or concentration - Percentile: Percentiles for data sets with 10 percent or more censored data (values less than the MRL) are estimated by log-probability regression (Helsel and Cohn, 1988). Concentrations are dissolved and in milligrams per liter unless otherwise specified. Abbreviations: MRL, minimum reporting level; µS/cm, microsiemens per centimeter at 25 degrees Celsius; CaCO₃, calcium carbonate; <, less than; µg/L, micrograms per liter]

	Measurement or concentration										
-				Percentile					Number of		
Constituent or property	Mini- mum	10	25	50 (Median)	75	90	Maxi- mum	Number of samples	samples below MRL (see <u>tables</u> <u>A1-A3</u>)		
Water temperature (degrees Celsius)	0.1	3.9	4.9	6.5	11.0	12.4	14.8	35	0		
Specific electrical conductance, (µS/cm)	39	50	62	75	92	96	99	35	0		
pH (units)	7.1	7.3	7.5	7.6	7.8	7.8	7.9	35	0		
Dissolved oxygen	9.4	10.4	10.8	11.8	12.4	12.75	13.7	34	0		
Ammonia nitrogen	<.015	< 0.015	< 0.015	0.011	0.02	0.025	0.05	35	24		
Ammonia-plus-organic nitrogen	<.1	<.1	<.1	<.1	<.1	<.1	.7	35	33		
Ammonia-plus-organic nitrogen, total	<.1	<.1	<.1	.06	.19	.62	2.3	35	25		
Nitrite nitrogen	<.01	<.01	<.01	<.01	.006	.01	.026	35	28		
Nitrite-plus-nitrate nitrogen	.054	.08	.12	.21	.25	.33	.39	35	0		
Phosphorus, total	<.01	<.01	<.01	.031	.144	.42	1.8	35	12		
Phosphorus	<.01	<.01	<.01	<.01	.007	.012	.02	35	32		
Orthophosphate phosphorus	<.01	<.01	<.01	<.01	.007	.011	.017	35	30		
Alkalinity (as CaCO ₃)	15	18	23	29	35	37	42	35	0		
Bicarbonate (as CaCO ₃)	18	21	28	36	42	45	51	35	0		
Calcium	4.7	5.5	7.0	8.8	11	11	12	34	0		
Magnesium	1.5	1.75	2.0	2.5	3.1	3.4	3.5	34	0		
Sodium	.9	1.0	1.2	1.4	1.9	2	2	34	0		
Potassium	.3	.32	.38	.4	.4	.5	.5	34	0		
Chloride	.4	.5	.7	.9	1.0	1.2	1.4	34	0		
Sulfate	2.3	3.1	4.2	6.3	7.5	9.8	12	34	0		
Fluoride	<.1	<.1	<.1	<.1	<.1	<.1	<.1	34	34		
Silica	4.6	5.6	6.6	7.6	8.6	8.95	9.3	34	0		
Iron, in μg/L	7.9	11	20	26	44	130	180	34	0		
Manganese, in µg/L	<4.0	4.4	5.0	6	7.7	13	17	34	1		
Dissolved solids, residue at 180 degrees Celsius	32	38	42	49	59	63	76	34	0		
Organic carbon	.2	.5	.95	1.4	2.35	3.5	5.4	33	0		
Organic carbon, suspended	<.1	.1	.2	.3	1.1	2.9	11	32	3		
Sediment, suspended	2	8	16	59	530	1,910	3,210	33	0		

In addition to monthly routine samples, about 25 percent of the samples at each of the three sites were collected during stormflow events. Maximum concentrations of total nitrogen, total phosphorus, and suspended sediment were observed in samples collected on the rising limb or near the peak of the hydrograph during runoff events, such as occurred in November 1995 and January, March, and October 1997 (figs. 16, 17, and 18). Concentrations of total nitrogen, total phosphorus, dissolved and suspended organic carbon, iron, and suspended sediment tended to vary directly with streamflow, as indicated by Kendall's τ , which ranged from 0.3 to 0.7 (table 9). Concentrations of dissolved solids and major ions, such as bicarbonate, varied inversely with streamflow ($\tau = -0.5$ to -0.7).

The high-flow period for the Nooksack River (figs. 12 and 14) is typically from October to February and for Fishtrap Creek from October to March (fig. 13). The transition period, from March to July in the mainstem, is also a period of high flows due to spring snowmelt; but in Fishtrap the transition period is from April to July and consists of diminishing flows as summer approaches. The low-flow period is August and September for the Nooksack and for Fishtrap. At all three sites, nutrient and suspended-sediment concentrations in samples collected in the high-flow period were generally higher than in samples collected in the transition and low-flow periods (figs. 16, 17, and 18).

Site 3: The water in the lower Nooksack was of generally good quality except for times when suspended-sediment concentrations were large or several pesticides and VOCs were present. Ten percent of the samples had suspended-sediment concentrations of 1,460 mg/L or higher, with a maximum of 2,890 mg/L observed on October 30, 1997. The sample collected on the rising limb of the hydrograph and near the peak of the October 30, 1997 storm also contained exceptionally high concentrations of total phosphorus (7.3 mg/L), total organic nitrogen (2.4 mg/L), and dissolved (5.5 mg/L) and suspended organic carbon (12.0 mg/L). Field notes on this day indicated considerable amounts of large, woody debris consisting of trees, logs, and root balls being transported by the river. On two occasions, the water temperature measured at the time of sample collection was 18.0°C (degrees Celsius), equal to the Washington State

standard for a Class A water body (see <u>table 2</u>). All nitrogen species analyzed were present in most samples; however, nitrate, with a median concentration of 0.35 mg/L, and total organic nitrogen, with a median of 0.13 mg/L, were the dominant nitrogen species (fig. 15).

Site 4: The water in Fishtrap was of fair quality. At times, iron, manganese, and fecal-indicator bacteria concentrations were large, and a number of pesticides and VOCs were present. In 11 samples, iron concentrations exceeded the USEPA SMCL of $300 \,\mu\text{g/L}$, and in 43 samples, manganese concentrations exceeded the SMCL of 50 µg/L (see table 2). In 14 samples collected from April 1997-August 1998, concentrations of Escherichia coli (E. coli) ranged from 87 to 5,900 col/100 mLs (colonies per 100 milliliters) (table 33, at back of report). Of these 14 samples, 8 had concentrations exceeding 298 col/100 mLs, USEPA's (1986b) recommended single-sample concentration for moderate, full-body contact recreation. Suspendedsediment concentrations in samples were low, with 90 percent of the concentrations less than 135 mg/L. Nitrate, with a median concentration of 2.8 mg/L, was the dominant nitrogen species (fig. 15).

Site 5: Water in the upper Nooksack was of generally high quality except at times when suspendedsediment concentrations were large. Ten percent of the samples had suspended-sediment concentrations greater than 1,900 mg/L and a maximum observed during the study of 3,210 mg/L on October 20, 1997. On one occasion, the concentration of dissolved oxygen measured at the time of sample collection was 9.4 mg/L and did not meet the Washington State standard of 9.5 mg/L concentration for a Class AA water body (see <u>table 2</u>). Nitrate, with a median concentration of 0.21 mg/L and total organic nitrogen, with a median of 0.06 mg/L (estimated by logprobability regression, Helsel and Cohn, 1988), were the dominant nitrogen species (fig. 15). The sample collected near the peak of the hydrograph during the storm on October 30, 1997, contained the highest concentration of total phosphorus (1.8 mg/L), total organic nitrogen (2.3 mg/L), and suspended organic carbon (11.0 mg/L) observed at this site during the study. Considerable amounts of large, woody debris were transported by the river during this storm.

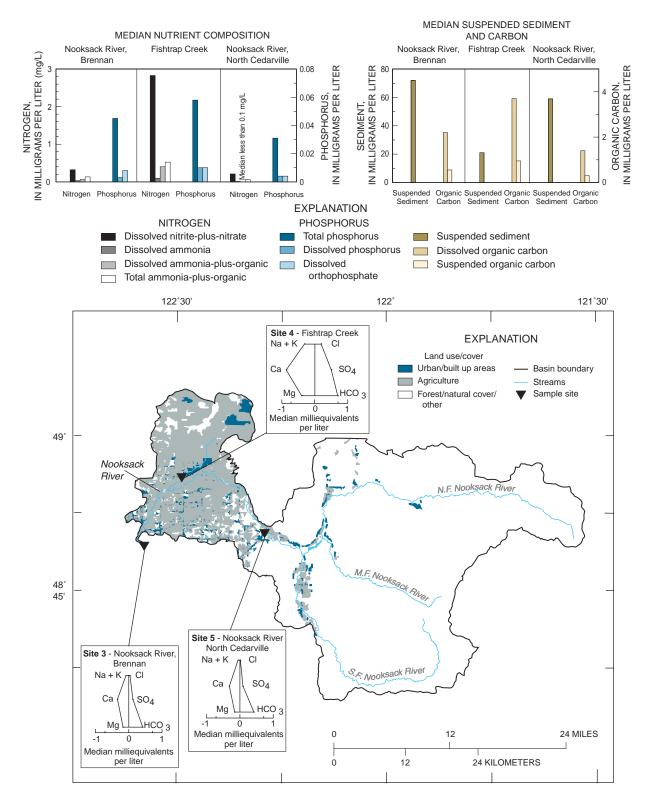


Figure 15. Median concentrations of nutrients, suspended sediment, organic carbon, and major ions in samples from the lower Nooksack River (site 3), Fishtrap Creek (site 4), and the upper Nooksack River (site 5) in the Puget Sound Basin study unit, Washington.

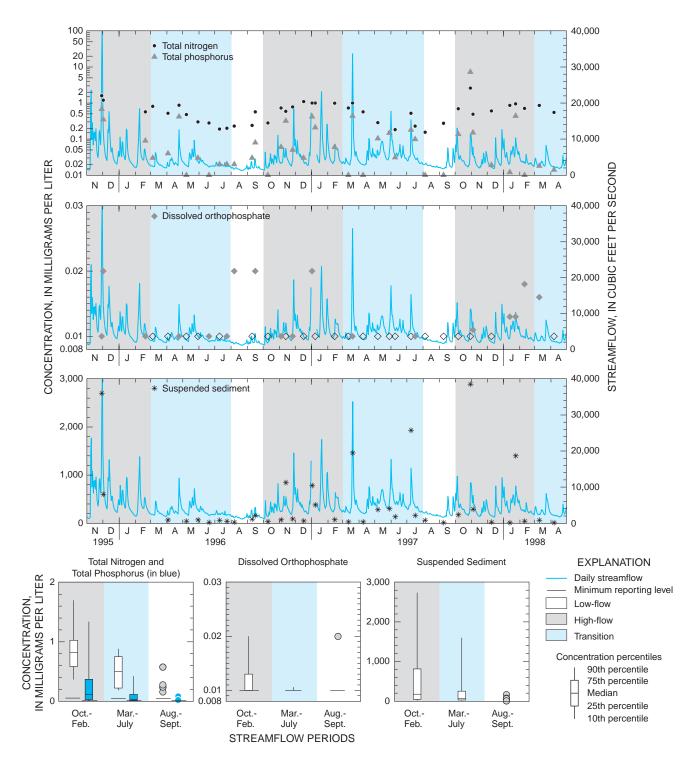


Figure 16. Time series of streamflow and concentrations of total nitrogen, total phosphorus, dissolved orthophosphate phosphorus, and suspended sediment in samples, and concentrations by three streamflow periods, for the lower Nooksack River (site 3) in the Puget Sound Basin study unit, Washington.

(Truncated boxplots of concentration percentiles require a minimum of nine observations, otherwise concentrations are plotted as individual points. Censored data in the time-series graphs are shown as an open symbol. Boxplots are truncated at the minimum reporting level indicated by solid line.)

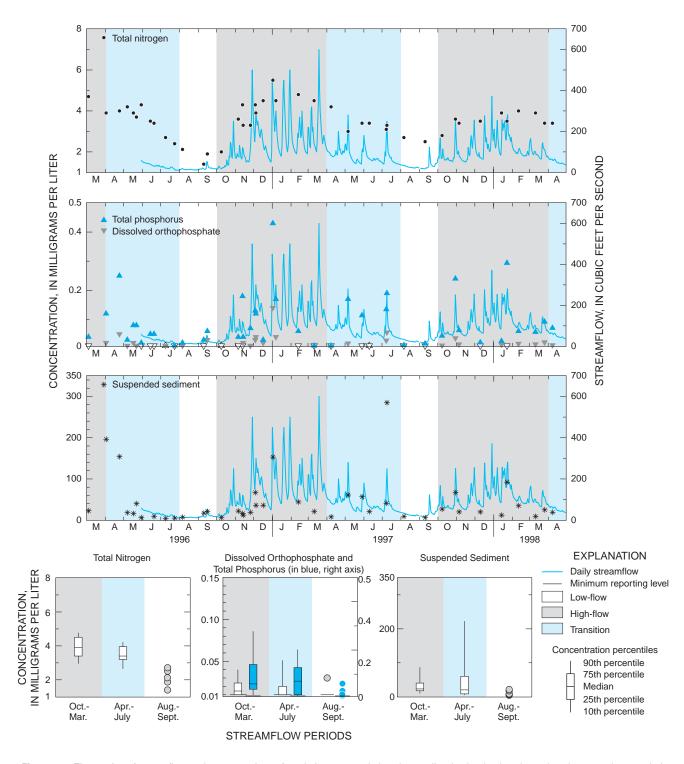


Figure 17. Time series of streamflow and concentrations of total nitrogen, total phosphorus, dissolved orthophosphate phosphorus, and suspended sediment in samples, and concentrations by three streamflow periods, for Fishtrap Creek (site 4) in the Puget Sound Basin study unit, Washington. (Truncated boxplots of concentration percentiles require a minimum of nine observations, otherwise concentrations are plotted as individual points. Censored data in the time-series graphs are shown as an open symbol. Boxplots are truncated at the minimum reporting level indicated by solid line.)

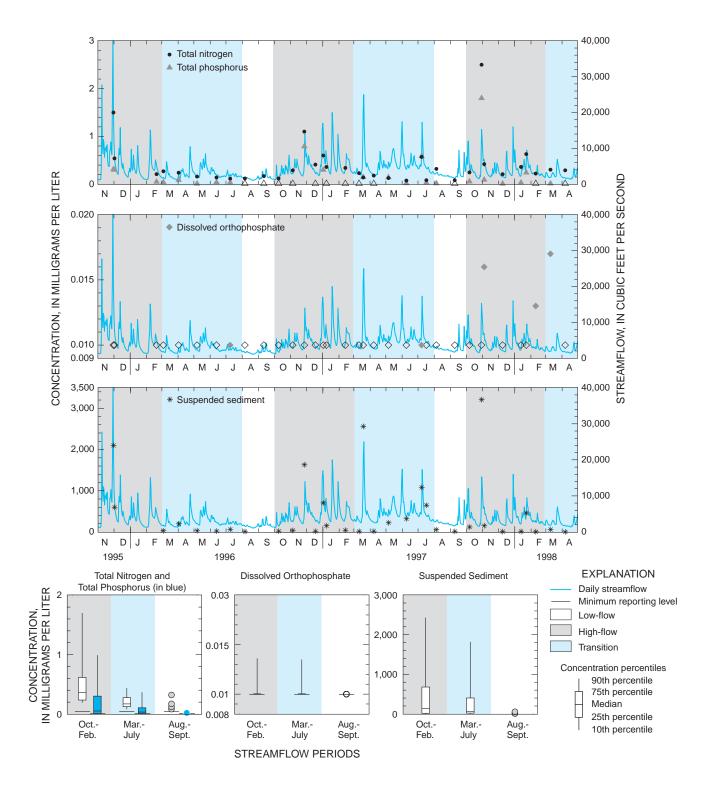


Figure 18. Time series of streamflow and concentrations of total nitrogen, total phosphorus, dissolved orthophosphate phosphorus, and suspended sediment in samples, and concentrations by three streamflow periods, for the upper Nooksack River (site 5) in the Puget Sound Basin study unit, Washington.

(Truncated boxplots of concentration percentiles require a minimum of nine observations, otherwise concentrations are plotted as individual points. Censored data in the time-series graphs are shown as an open symbol. Boxplots are truncated at the minimum reporting level indicated by solid line.) **Table 9.**Correlation between selected water-quality characteristics or chemical constituents and streamflow for the lowerNooksack River (site 3), Fishtrap Creek (site 4), and the upper Nooksack River (site 5) in the Puget Sound Basin study unit,Washington

Madan and literations denied	Kend	all's tau correlation coeff	icient
Water-quality characteristic or chemical constituent	Lower Nooksack River (Site 3)	Fishtrap Creek (Site 4)	Upper Nooksack Rive (Site 5)
Specific electrical conductance	-0.55	-0.49	-0.65
Dissolved solids	47	47	53
Total nitrogen	.37	.41	35
Dissolved nitrite-plus-nitrate nitrogen	05	.12	.05
Total ammonia-plus-organic nitrogen	.47	.70	.38
Dissolved ammonia-plus-organic nitrogen	.06	.64	.18
Total phosphorus	.67	.59	.58
Dissolved orthophosphate phosphorus	.12	.44	<.01
Dissolved organic carbon	.57	.58	.45
Suspended organic carbon	.59	.49	.53
Suspended sediment	.73	.62	.73
Bicarbonate	57	70	61
Iron	.37	.35	.49
Manganese	.08	.21	.19

Nooksack River Basin Organic Chemistry

Pesticides detected in water samples from site 3 and site 4 in the Nooksack River Basin were mostly herbicides, of which atrazine and simazine were most frequency detected. Of the 86 pesticides analyzed for, diazinon, carbaryl, ethoprophos, and malathion were among the few insecticides detected. Nearly all of the pesticides detected in samples from site 3 on the lower Nooksack, which integrates all the water in the basin, were also detected in samples from site 4 on Fishtrap Creek. However, fewer types of pesticides (only about one-half the number) were detected at site 3 than at site 4. This suggests that, in addition to analyte losses due to processes such as transformation or sedimentation, pesticides reaching the river from tributaries like Fishtrap Creek or from adjacent land areas are diluted to concentrations below detection levels by the large volume of water in the river. The pesticides found most frequently in the Nooksack River Basin were consistent with pesticides found most frequently in study units

across the nation and included atrazine, simazine, diazinon, and carbaryl (Larson and others, 1997). Most concentrations of the frequently detected pesticides in the Nooksack River Basin ranked within or below the middle 50-percent range of concentrations in mixed land-use river basins studied nationwide in 36 NAWQA study units during 1991–98 (Ebbert and others, 2000).

Site 3: In the lower Nooksack, 16 pesticide compounds were found in samples collected from March 1996 through July 1997. The most frequently detected pesticide, atrazine, was in 15 of 22 samples at concentrations as high as 0.042 μ g/L (table 10). The herbicides simazine and metolachlor were in the next most frequently detected pesticides. The insecticides diazinon, ethoprophos, and malathion were detected in one to two samples and in low concentrations near laboratory MRLs. Detections and higher concentrations of pesticides tended to coincide with the rainy season from October through February (fig. 19).

Table 10. Pesticides in water samples from the lower Nooksack River (site 3) in the Puget Sound Basin study unit, Washington

[Water-quality criteria – Drinking water: U.S. Environmental Protection Agency (1996). Aquatic organisms – Chronic (USGS): U.S. Geological Survey (1999a). Based on 22 samples collected March 1996 to July 1997; all concentrations are in micrograms per liter (µg/L); method detection limits are from reports by Zaugg and others (1995), Lindley and others (1996), Werner and others (1996), and U.S. Geological Survey National Water Quality Laboratory Technical Memorandums 98.03A and 96.06A; MCL, maximum contaminant level; HAL, Health advisory level; ^E, Estimated — a qualitative value that is less than the statistically determined method detection limit of lowest calibration standard; –, no value or data]

			Median	concen- detection	Water-quality criteria						
Pesticide	Number of		concen-		Drinkir	ıg water	Aquatic organisms (freshwater)				
	Pesticide Interior concentration value tration tration detected cetochlor 1 0.006 - trazine 15 $.042$ 0.016 trazine 15 $.042$ 0.016 trazine 6 $E.005$ $E.004$ tazinon 1 $.005$ - toron 1 $.005$ - toron 1 $.008$ - uometuron 1 $.008$ - alathion 2 $E.004$ $E.002$ CPA 1 $E.02$ - apropamide 1 $.0085$ - ometon 1 $E.01$ - <th>limit</th> <th>MCL</th> <th>HAL</th> <th>Acute</th> <th>Chronic</th> <th>Chronic (USGS)</th>	limit	MCL	HAL	Acute	Chronic	Chronic (USGS)				
Acetochlor	1	0.006	_	0.002	-	_	_	_	_		
Atrazine	15			.001	3	3	¹ 70	$^{1}7$	1.8		
Deethylatrazine	6	^E .005	^E .004	.002	_	-	-	-	-		
Diazinon	1	.005	-	.002	_	0.6	² 0.16	² 0.04	0.08		
Diuron	1	^E .002	_	.02	_	10	-	_	_		
Ethoprophos	1	.019	-	.003	_	-	-	-	-		
Fluometuron	1	.08	_	.035	_	90	-	_	_		
Malathion	2	^E .005	_	.005	_	200	-	³ .1	.1		
Metolachlor	7	^E .004	E.002	.002	_	70	-	_	7.8		
MCPA	1	^E .02		.17	_	10	-	_	2.6		
Napropamide	1	.006	_	.003	_	_	-	_	_		
Norflurazon	1	^E .17	_	.024	_	_	-	_	-		
Pebulate	1	.085	_	.004	_	_	-	_	-		
Prometon	1	^E .01	_	.018	_	100	-	_	-		
Simazine	9	.024	^E .004	.005	4	4	¹ 100	¹ 10	10		
Tebuthiuron	1	.087	_	.01	_	500	-	_	1.6		
Terbacil	1	^E .092	_	.007	_	90	_	_	_		

¹Norris and Dost (1992).

²Menconi and Cox (1994).

³U.S. Environmental Protection Agency (1998).

For example, metolachlor and deethylatrazine, compounds not detected in samples during low-flow conditions, were detected in samples during the wet season or during storm events. Atrazine and simazine varied somewhat directly with streamflows, but the relations were weak (Kendall's $\tau = 0.4$; p-values less than 0.05). The three pesticides found in samples from site 3 but not from site 4—fluometuron, MCPA, and norflurazon—each occurred in only one sample: MCPA in a June sample, and fluometuron and norflurazon together in a February sample. MCPA is used for a variety of agricultural and non-agricultural purposes; however, the purpose for which fluometuron (commonly used for weed control in cotton) is used in the PSB is unknown. Norflurazon is applied to blueberries or raspberries (see table 27). No pesticide concentration exceeded established drinking-water or aquatic-life criteria concentrations.

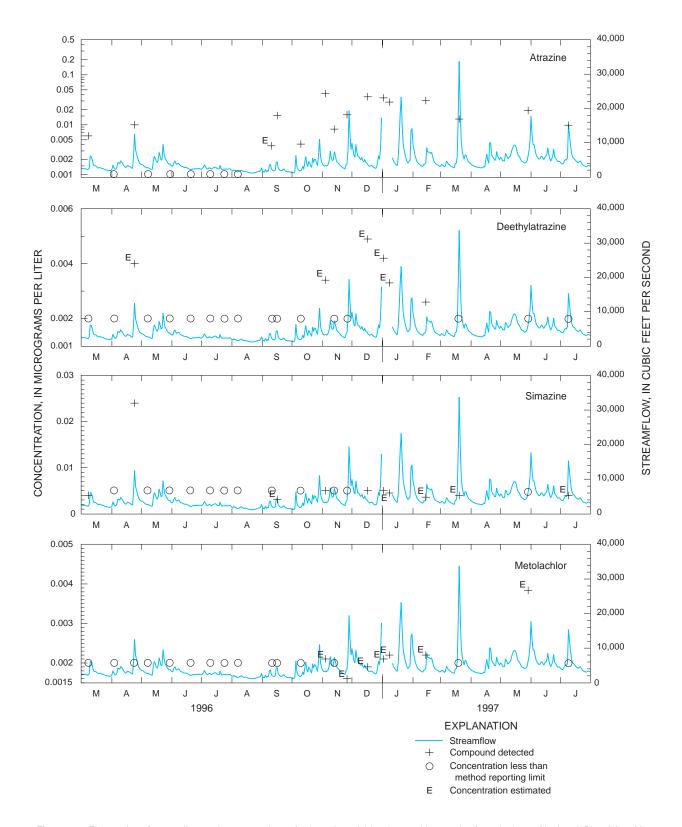


Figure 19. Time series of streamflow and concentrations of selected pesticides detected in samples from the lower Nooksack River (site 3) in the Puget Sound Basin study unit, Washington.

Out of 86 VOCs analyzed for, 15 were detected in samples from site 3 (<u>table 11</u>). Carbon disulfide was the most frequently detected compound with 15 detections in 21 samples; however, none of the concentrations was above the 1999 LRLs. Only methylbenzene was detected at concentrations above the LRL. None of the concentrations of VOCs in the samples exceeded maximum concentrations specified in drinking-water or aquatic-life criteria. Methylbenzene concentrations showed some correspondence with the season of the year, with the highest concentrations observed during late fall and early winter (<u>fig. 20</u>), and did not relate to streamflow. No patterns with season or magnitude of streamflow could be discerned for the other 14 compounds detected in samples.

Table 11. Volatile organic compounds in water samples from the lower Nooksack River (site 3) in the Puget Sound Basin study unit, Washington

[Water-quality criteria – Drinking water: U.S. Environmental Protection Agency (1996). Based on 21 samples collected March 1996 to July 1997; all concentrations are in micrograms per liter (μ g/L); MRL, method reporting level (Connor and others; 1998); LRL, laboratory reporting level; MCL, maximum contaminant level; HAL, health advisory level; ^E, Estimated–a qualifier for an analytical result based on the long-term method detection level, laboratory reporting level, and lowest calibration standard (Childress and others, 1999); –, no value or data]

		Percentage				Wa	ater-quality	criteria
Volatile organic compound	Number of detections	of detec- tions above 1999 LRL and (number)	Maximum concen- tration value	Median concen- tration detected	MRL (1999 LRL)	Drinking water		Aquatic organisms (freshwater)
		(number)				MCL	HAL	Chronic
1,2,4-Trimethylbenzene	3	0	E0.01	E0.008	0.056 (0.056)	_	_	_
1,2-Dimethylbenzene (o-Xylene)	3	0	^E .01	^E .01	.064 (.06)	10,000	10,000	_
1,3-plus-1,4-Dimethylbenzene (<i>m</i> , <i>p</i> -Xylene)	5	0	^E .03	^E .01	.064 (.06)	10,000	10,000	_
2-Butanone (Methyl ethyl ketone)	2	0	^E .3	_	1.65 (1.6)	_	_	_
1-Isopropyl-4-methylbenzene (p-Isopropyltoluene)	4	0	^E .007	^E .005	.11 (.11)	-	-	_
Acetone	7	0	E2.8	^E 1.3	4.904 (5)	-	_	-
Benzene	1	0	^E .04	-	.032 (.1)	5	-	¹ 370
Bromoform	1	0	^E .008	-	.104 (.1)	100	-	_
Carbon disulfide	15	0	^E .1	^E .01	.08 (.37)	_	_	_
Chloromethane (Methyl chloride)	11	0	^E .08	^E .04	.254 (.25)	_	3	_
Ethenylbenzene (Styrene)	1	0	E.001	_	.042 (.042)	100	100	_
Ethylbenzene	3	0	^E .01	^E .009	.03 (.03)	700	700	¹ 90
Methylbenzene (Toluene)	14	79 (11)	.34	.09	.038 (.05)	1,000	1,000	¹ 2
Naphthalene	1	0	^E .008	-	.25 (.25)	-	20	¹ 1.1
Trichloromethane (Chloroform)	3	0	^E .007	^E .007	.052 (.052)	100	_	¹ 1.8

¹Environment Canada, 1999

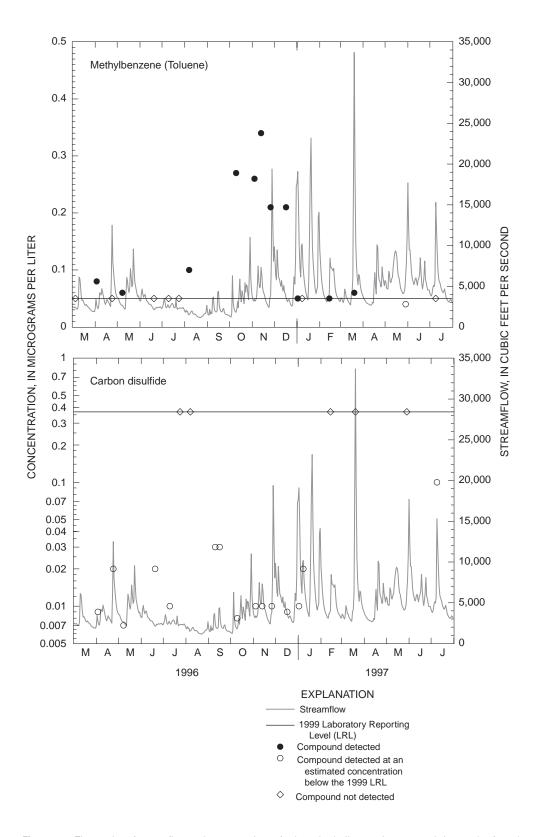


Figure 20. Time series of streamflow and concentrations of selected volatile organic compounds in samples from the lower Nooksack River (site 3) in the Puget Sound Basin study unit, Washington.

Site 4: In Fishtrap, 29 pesticides were found in samples collected from March 1996 through September 1997. The herbicides atrazine and simazine and the transformation product deethylatrazine were detected most frequently, each found in 31 of 32 samples (table 12). Median concentrations of these three compounds were 0.056, 0.017, and 0.006 μ g/L, respectively (table 12). The herbicides prometon and tebuthiuron were the next most frequently detected pesticides. Of the 29 pesticides detected, 7 were insecticides-carbaryl, carbofuran, diazinon, ethoprophos, malathion, oxamyl, and propargite. Diazinon was detected in 44 percent of the samples in concentrations ranging from 0.004 to 0.133 μ g/L. Five samples had diazinon concentrations exceeding $0.04 \mu g/L$, a limit recommended by Menconi and Cox (1994) for the protection of aquatic life (see table 2). Carbaryl was detected in three samples and all three had concentrations exceeding 0.017 µg/L, a limit recommended by Norris and Dost (1992) for the protection of aquatic life.

Most pesticide detections and concentrations in samples at site 4 did not correspond to streamflow. Atrazine, deethylatrazine, and simazine concentrations tended to vary directly with streamflow, but the relations were weak (Kendall's τ ranged from 0.3 to 0.4; p-values less than 0.01). The timing of applications appeared to influence detections and concentrations of certain pesticides such as diazinon. Diazinon was often detected, sometimes in high concentrations, from approximately April through June, corresponding to the season when application rates are generally highest. Some of the largest concentrations for pesticides such as simazine, prometon, and diazinon were in samples collected during storm runoff events. Perhaps because of different application procedures or treated land areas, tebuthiuron and oxamyl were detected in several samples collected during May–July 1996, but were not in the few samples during May–July 1997 (<u>fig. 21</u>).

Eighteen VOCs were detected at site 4 (table 13). Chloromethane was most frequently observed with 22 detections in 32 samples, but all of these detections were below the 1999 LRL. Six compoundschlorobenzene, ethylbenzene, dichloromethane, methylbenzene, 1,3-plus-1,4-dimethylbenzene (m,pxylene), and 1,2-dimethylbenzene (o-xylene)—were detected at concentrations above the LRL. Of these six compounds, methylbenzene was detected most frequently (85 percent of the 20 samples with detections) at concentrations above the LRL. The remaining five compounds were detected only once each at a concentration above the LRL. None of the VOC concentrations was above any of the established drinking-water standards or aquatic-life criteria. The presence of methylbenzene, methyl tert-butyl ether (MTBE), and 1,3-plus-1,4-dimethylbenzene in surface water tended to correspond with elevated streamflows between October and March (fig. 22). These compounds generally were not detected during baseflow conditions between June and September except for one low-level detection of MTBE. MTBE is used year-round in Canada as a fuel-additive to gasoline (Duncan Ferguson, B.C. Environment, oral commun., 1999), but it is likely that the detections only appear during the winter, because the solubility of MTBE increases with decreasing temperatures (Lopes and Bender, 1998).

Table 12. Pesticides in water samples from Fishtrap Creek (site 4) in the Puget Sound Basin study unit, Washington

[Water-quality criteria – Drinking water: U.S. Environmental Protection Agency (1996). Aquatic organisms – Chronic (USGS): U.S. Geological Survey (1999a). Based on 32 samples collected March 1996 to September 1997; all concentrations are in micrograms per liter (μ g/L); bold type indicates value above aquatic life criterion; method detection limits are from reports by Zaugg and others (1995), Lindley and others (1996), Werner and others (1996), and U.S. Geological Survey National Water Quality Laboratory Technical Memorandums 98.03A and 96.06A; MCL, maximum contaminant level; HAL, Health advisory level; ^E, Estimated–a qualitative value that is less than the statistically determined method detection limit or lowest calibration standard; –, no value or data]

			Median		Water-quality criteria						
Pesticide	Number of	Maximum concentration	concen-	Method detection	Drinkin	g water	Aquatic	organisms (fi	reshwater)		
Pesticide dei Acetochlor Alachlor Atrazine Carbaryl Carbofuran 2,4-D DCPA Deethylatrazine Diazinon Dichlobenil Diuron EPTC Ethoprophos Linuron Malathion Metolachlor Metribuzin Molinate	detections	value	tration detected	limit	MCL	HAL	Acute	Chronic	Chronic (USGS)		
Acetochlor	4	0.137	0.010	0.002	_	_	-	_	-		
Alachlor	2	.19	-	.002	2	-	-	-	-		
Atrazine	31	1.4	.056	.001	3	3	¹ 70	¹ 7	1.8		
Carbaryl	3	^E .133	^E .074	.003	_	700	¹ 0.17	$^{1}0.017$	0.2		
Carbofuran	1	^E .005	-	.003	40	40			1.8		
2,4-D	1	.32	-	.15	70	70	¹ 10	¹ 1	4		
DCPA	2	^E .003	-	.002	-	-	-	-	-		
Deethylatrazine	31	^E .014	^E .006	.002	-	-	-	-	-		
Diazinon	14	.113	.013	.002	-	0.6	² .16	² .04	.08		
Dicamba	1	^E .03	_	.035	_	200	¹ 390	¹ 39	10		
Dichlobenil	2	^E .01	_	1.2	_	_	-	_	_		
Diuron	2	.44	_	.02	_	10	-	_	_		
EPTC	6	.026	.005	.002	_	_	-	_	_		
Ethoprophos	2	.013	_	.003	_	_	-	_	_		
Linuron	3	.32	.12	.002	_	_	-	_	7		
Malathion	1	.025	_	.005	_	200	-	³ .1	.1		
Metolachlor	14	.037	.004	.002	_	70	-	_	7.8		
Metribuzin	2	.025	_	.004	_	100	-	_	1.0		
Molinate	1	.005	_	.004	_	_	-	_	_		
Napropamide	7	.1	.03	.003	_	_	-	_	_		
Oryzalin	1	.04	_	.31	_	_	-	_	_		
Oxamyl	11	.16	.12	.018	200	200	-	_	_		
Pebulate	2	.08	_	.004	_	_	-	_	_		
Prometon	22	.087	^E .006	.018	_	100	_	_	_		
Pronamide	1	^E .004	_	.003	_	50	_	_	_		
Simazine	31	1.0	.017	.005	4	4	¹ 100	¹ 10	10		
Tebuthiuron	21	.095	.012	.01	_	500	_	_	1.6		
Terbacil	2	^E .077	_	.007	_	90	_	_	_		
Trifluralin	1	.005	_	.002	_	5	_	_	.2		

¹Norris and Dost (1992).

²Menconi and Cox (1994).

³U.S. Environmental Protection Agency (1998).

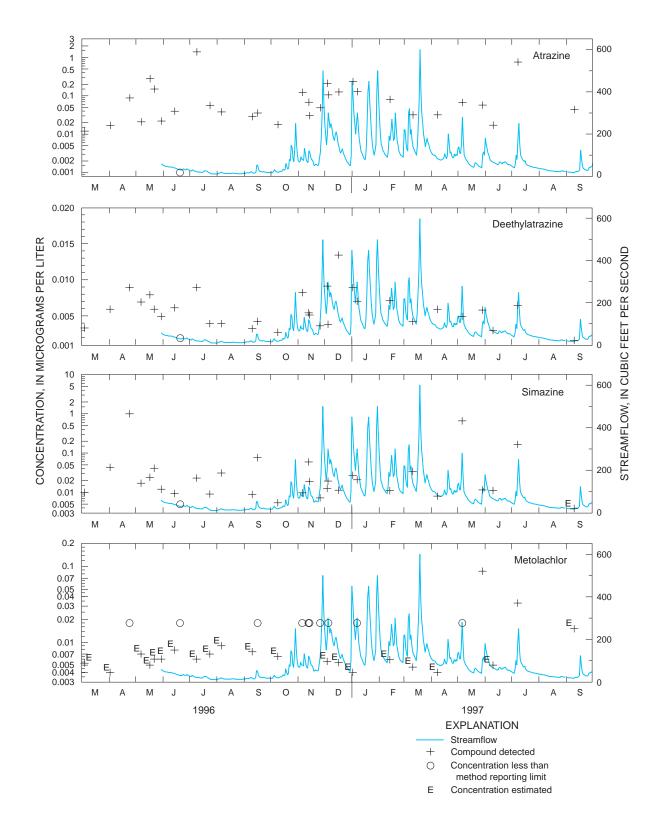


Figure 21. Time series of streamflow and concentrations of selected pesticides detected in samples from Fishtrap Creek (site 4) in the Puget Sound Basin study unit, Washington.

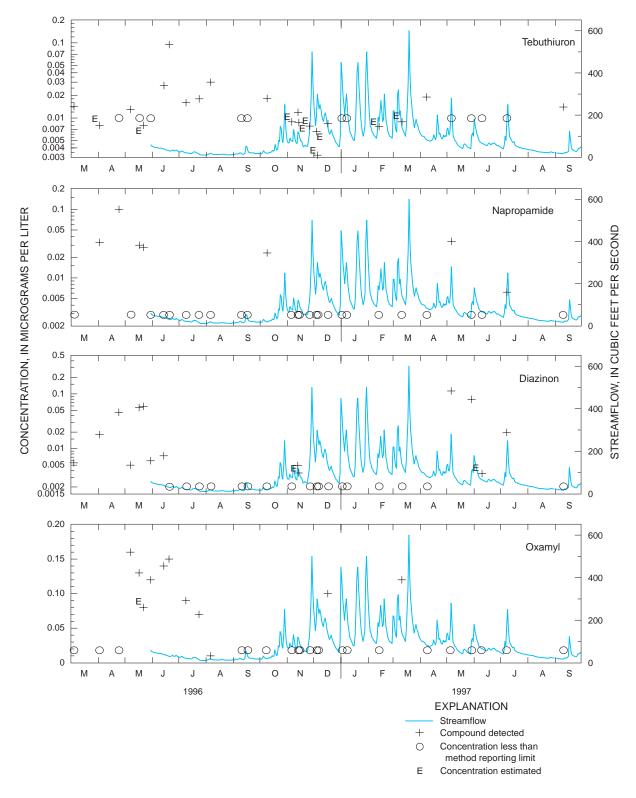




Table 13. Volatile organic compounds in water samples from Fishtrap Creek (site 4) in the Puget Sound Basin study unit, Washington

[Water-quality criteria – Drinking water: U.S. Environmental Protection Agency (1996). Based on 32 samples collected between March 1996 to September 1997; all concentrations are in micrograms per liter (μ g/L); MRL, method reporting level (Connor and others; 1998); LRL, laboratory reporting level; MCL, maximum contaminant level; HAL, health advisory level; ^E, Estimated–a qualifier for an analytical result based on the long-term method detection level, laboratory reporting level, and lowest calibration standard (Childress and others, 1999); –, no value or data.]

		Percentage of				Water-quality criteria			
Volatile organic compound	Number of detections	detections above 1999 LRL and	Maximum concen- tration value	Median concen- tration detected	MRL (1999 LRL)	Drinking water		Aquatic organisms (freshwater)	
		(number)				MCL	HAL	Chronic	
1,2,4-Trimethylbenzene	4	0	E0.02	0.0145	0.056 (0.056)	_	I	_	
1,2-Dichloropropane	7	0	^E .03	^E .02	.068 (.068)	5	_	_	
1,2-Dimethylbenzene (o-Xylene)	1	100 (1)	^E .09	-	.064 (.06)	10,000	10,000	-	
1,3-plus-1,4-Dimethylbenzene (<i>m</i> , <i>p</i> -Xylene)	5	20 (1)	^E .1	^E .02	.064 (.06)	10,000	10,000	-	
2-Butanone (Methyl ethyl ketone)	7	0	^E 1.4	^E .6	1.65 (1.6)	-	-	_	
1-Isopropyl-4-methylbenzene (p-Isopropyltoluene)	1	0	^E .006	-	.11 (.11)	_	-	_	
Acetone	8	0	^E 3.2	1.8	4.904 (5)	_	_	_	
Benzene	2	0	^E .1	-	.032 (.1)	5	_	¹ 370	
Carbon disulfide	14	0	^E .03	^E .015	.08 (.37)	_	_	_	
Chlorobenzene	1	100 (1)	^E .03	-	.028 (.028)	100	100	¹ 1.3	
Chloromethane (Methyl chloride)	22	0	^E .1	^E .05	.254 (.25)	_	3	_	
Dichloromethane (Methylene chloride)	2	50 (1)	^E 1.6	-	.382 (.38)	5	_	¹ 98.1	
Diethyl ether	1	0	^E .09	-	.17 (.17)	-	-	_	
Ethenylbenzene (Styrene)	1	0	^E .01	-	.042 (.042)	100	100	_	
Ethylbenzene	3	33 (1)	^E .06	^E .003	.03 (.03)	700	700	¹ 90	
Methylbenzene (Toluene)	20	85 (17)	.35	^E .01	.038 (.05)	1,000	1,000	¹ 2	
Methyl tert-butyl ether (MTBE)	6	0	^E .09	^E .035	.054 (.17)	_	20	_	
Trichloromethane (Chloroform)	9	0	^E .01	E.008	.052 (.052)	100	_	¹ 1.8	

¹Environment Canada (1999).

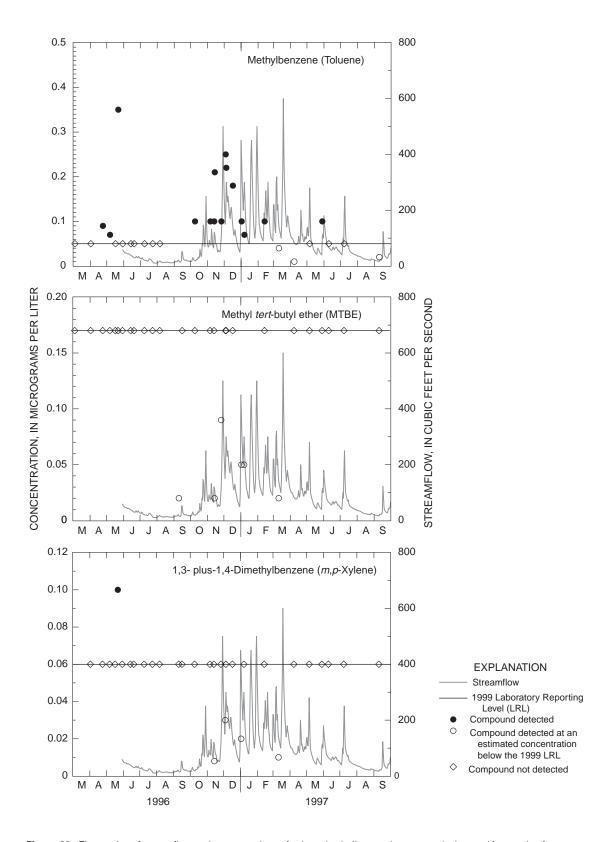


Figure 22. Time series of streamflow and concentrations of selected volatile organic compounds detected in samples from Fishtrap Creek (site 4) in the Puget Sound Basin study unit, Washington.

Green-Duwamish River Basin

The Green-Duwamish River originates as the Green River within the Cascade Range physiographic province and flows about 24 miles through forested mountainous terrain into Howard A. Hanson Reservoir, which is formed by Howard A. Hanson Dam at river mile 64.5 (see <u>fig. 1</u>). Below the dam at about river mile 59, the Green River enters the Puget Sound Lowlands physiographic province. The remaining 48 miles of the Green River drains the Puget Sound Lowlands and flows through a region of increasingly intensive agricultural and urban land use. At river mile 11, the Green becomes the Duwamish River, which flows through some of the more industrialized areas of the study unit and then enters Puget Sound. Five basic fixed sites were established in the Green-Duwamish River Basin (fig. 1 and table 1): Site 6 on the Duwamish, site 7 on Springbrook Creek, site 8 on Big Soos Creek, site 9 on Newaukum Creek, and site 10 on the upper Green River. Site 6 is an integrator of the quality of water from the Green-Duwamish River Basin, consisting of high-altitude mountains with snowfields and forests, regions with a few small population centers below the dam, and agricultural, commercial/industrial, and residential land uses in the Lowlands. The river at site 6 drains an area of 461 mi^2 . Site 7 is an indicator of commercial/industrial and residential urban land use within a drainage area of 20 mi². Site 8 is an indicator of an urban/suburban basin rapidly changing from a more rural and forested basin. Big Soos at site 8 drains an area of 66.7 mi². Site 9 is an indicator of a largely agricultural basin consisting mostly of dairy, cattle, and small horse farms, but also with a fair amount of suburban development within a drainage area of 27.4 mi². Site 10 is an indicator of water quality from forest practices and from undisturbed regions of the upper Green River Basin. The river at site 10 drains an area of 16.5 mi^2 .

Green-Duwamish River Basin Hydrology

Annual streamflows for water years 1996 and 1997 were greater than mean annual flows for the periods of record at sites 6, 8, 9, and 10 (see <u>fig. 4</u>). Annual flows for 1998 were less than the mean annual flows, but were within the interquartile range of flows at these four sites. No long-term record existed at Springbrook (site 7) for comparing annual or daily flows observed during the study. Flow variability in Springbrook as it related to climate during the sampling period is illustrated by the daily-streamflow hydrograph for this study. Precipitation recorded at SeaTac International Airport in amounts above normal from October 1995 through February 1996 (see fig. 3) contributed to above-normal streamflows from November 1995 through February 1996. The storms in early February 1996 generated the highest daily flows observed during the 3-year study period at sites 6-9 (figs. 23, 24, 25, and 26) and the second highest daily flow observed at site 10 (fig. 27). Except for some high flows caused by late April-early May storms, daily flows from spring through fall were mostly within the interquartile range of flows for each site except at site 10. At site 6, relatively normal flows were due in part to flow regulation at Howard A. Hanson Dam. At site 10, summer daily flows were low, in that most were at or below the 25th percentile in magnitude (fig. 27).

In water year 1997, streamflows were mostly normal or above normal. At the end of December, a storm brought freezing rain and snow to the lower elevations. The Seattle-Tacoma area received about 2 feet of snow. Following the snowfall, warmer temperatures and heavy rain from December 30 through January 1, known locally as the New Year's Day 1997 storm, melted the snow and raised several lowland streams to flood levels. Rainfall in amounts up to more than twice normal during December 1996 and during the regional storm of March 18–20, 1997, generated high flows at all five sites. Most daily streamflows from late spring into early fall were above the 75th quartile because of above-normal rainfall amounts.

Daily streamflows continued to be above normal at the start of water year 1998. From winter into early spring 1998, daily flows were mostly within the interquartile range. With precipitation only 40 percent of normal for the month of April, daily flows dropped below normal and remained below the 25th quartile to the end of the study period at the end of April 1998.

Magnitudes of streamflows at the time of sample collection at sites 6, 8, 9, and 10 spanned a wide range, from high flows that are exceeded less than 1 percent of the time to low flows that are exceeded more than 90 percent of the time (figs. 25, 25, 26, and 27). Sample collections were fairly evenly distributed over the range of flows that can occur at these sites. Two sets of storm

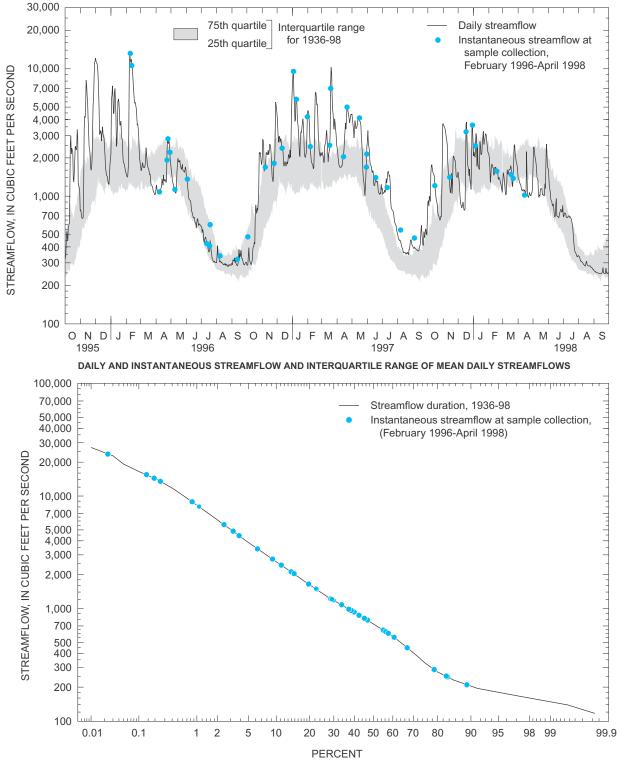
samples (one near the hydrograph peak and one on the falling limb of the hydrograph) were collected at sites 6–9 during the New Year's Day 1997 storm, which resulted in the second highest daily flows observed at these four sites during the study period. Samples were collected at all five sites in the basin during the March 1997 regional storm.

Site 6: For the Duwamish River, estimated average annual streamflow based on 32 years of record at the gage upstream (12113000, Green River near Auburn) was 1,480 ft³/s, which was exceeded by the annual flows for 1996 and 1997, but not for 1998. Estimated annual flows for water years 1996, 1997, and 1998 were 2,060, 2,090, and 1,220 ft³/s, respectively. In water year 1996, samples were collected on February 8, 1996, when the highest daily flow observed at this site during the study, more than 11,000 ft³/s, occurred. In water year 1997, the New Year's Day 1997 storm brought the river to a little over 9,000 ft³/s by January 2, 1997.

Site 7: For Springbrook, the average streamflow estimated using 3 years of record at two upstream gages (12113346, Springbrook Creek near Orillia, and 12113349, Mill Creek near Mouth) was 42 ft³/s. Estimated annual flows for water years 1996 and 1997 were 48 and 45 ft³/s, respectively. The 1998 estimated flow was 33 ft³/s. The February 1996 storms brought the creek to about 820 ft³/s, the maximum daily flow observed during the study. The New Year's Day 1997 storm event produced the second highest daily flow, 530 ft³/s, for the study period. Site 8: Mean annual streamflow for Big Soos for 32 years of record was 125 ft³/s, which was exceeded by annual flows of 168 and 195 ft³/s for water years 1996 and 1997, respectively. The 1998 annual flow was 110 ft³/s. The February 1996 storm brought the creek to 3,580 ft³/s, its maximum recorded daily flow for the period of record. The daily flow of 1,370 ft³/s during the New Year's Day 1997 storm was a peak discharge for 1997.

Site 9: Mean annual streamflow for Newaukum for 52 years of record was 60 ft³/s, which was exceeded by annual flows of 80.8 and 83.7 ft³/s for water years 1996 and 1997, respectively. The annual flow for 1998 was 51.9 ft³/s. The heavy rainstorms in February 1996 resulted in a flow of 1,670 ft³/s on February 9, which was the highest recorded daily flow for the period of record at this site. Daily flow during the New Year's Day 1997 storm reached a maximum of 679 ft³/s.

Site 10: Although the period of record for site 10 is only 6 years, annual and daily flows were compared to the mean annual and the interquartile range of flows for this study. Based on 6 years of record, the mean annual streamflow for the upper Green was 57.8 ft³/s, which was exceeded by the annual flows for 1996 and 1997, but not for 1998. Annual flows for water years 1996, 1997, and 1998 were 79.0, 81.4, and 50.1 ft³/s, respectively. Storms in November and February brought the river to more than $1,000 \text{ ft}^3/\text{s}$, the maximum recorded daily flow for the period of record. In water year 1997, above-normal precipitation resulted in a flow of 465 ft^3/s , the second highest daily flow observed at this site during the study. One storm sample collected early in water year 1998 (on October 30, 1997) was during a storm that generated a peak discharge for 1997.



PERCENTAGE OF TIME STREAMFLOWS ARE EQUALED OR EXCEEDED AND INSTANTANEOUS STREAMFLOW

Figure 23. Daily and instantaneous streamflow at the time of sample collection, interquartile range of mean daily streamflows for the period of record, and percentage of time streamflows are equaled or exceeded at the Duwamish River (site 6) in the Puget Sound Basin study unit, Washington.

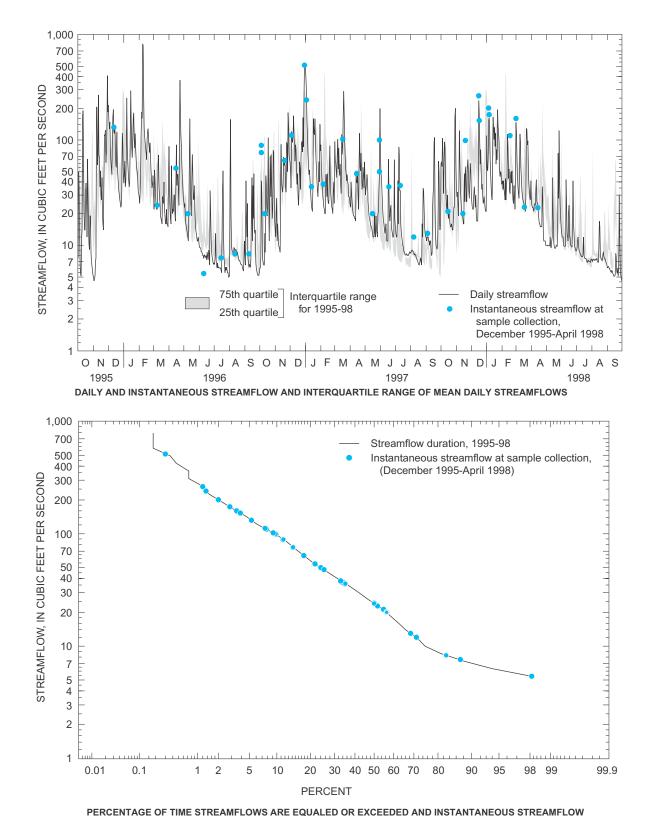
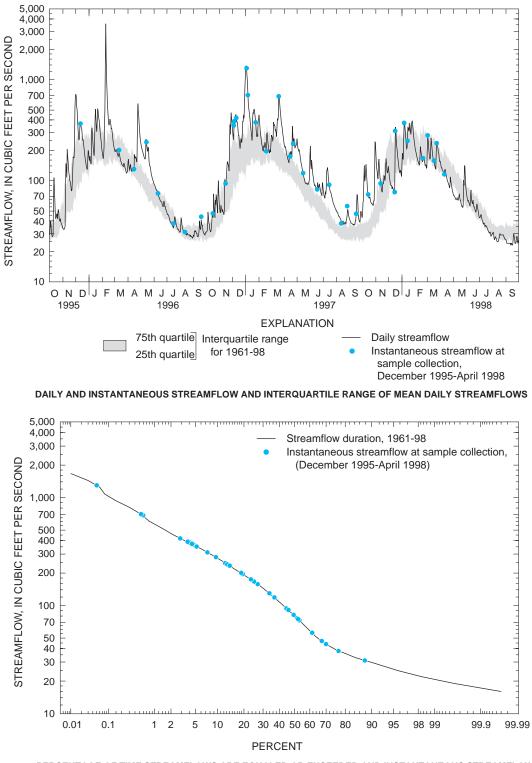
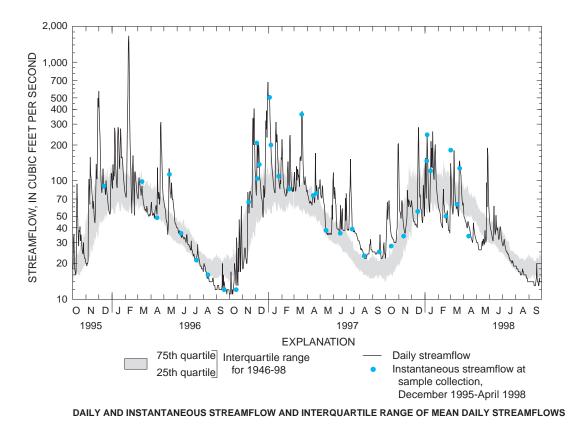


Figure 24. Daily and instantaneous streamflow at the time of sample collection, interquartile range of mean daily streamflows for the period of record, and percentage of time streamflows are equaled or exceeded at Springbrook Creek (site 7) in the Puget Sound Basin study unit, Washington.



PERCENTAGE OF TIME STREAMFLOWS ARE EQUALED OR EXCEEDED AND INSTANTANEOUS STREAMFLOW

Figure 25. Daily and instantaneous streamflow at the time of sample collection, interquartile range of mean daily streamflows for the period of record, and percentage of time streamflows are equaled or exceeded at Big Soos Creek (site 8) in the Puget Sound Basin study unit, Washington.



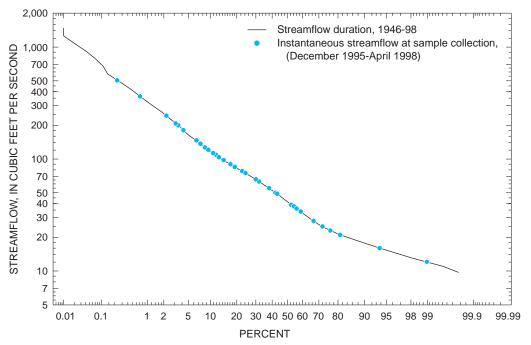
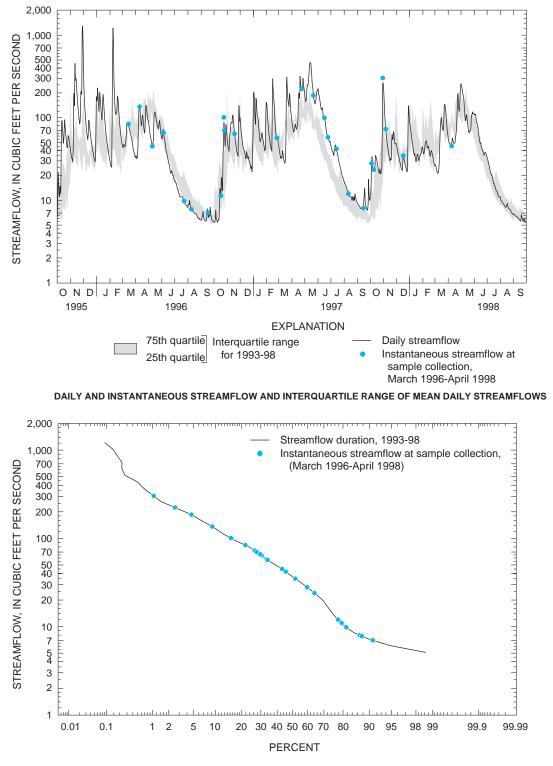




Figure 26. Daily and instantaneous streamflow at the time of sample collection, and the interquartile range of mean daily streamflows for the period of record, and percentage of time streamflows are equaled or exceeded at Newaukum Creek (site 9) in the Puget Sound Basin study unit, Washington.



PERCENTAGE OF TIME STREAMFLOWS ARE EQUALED OR EXCEEDED AND INSTANTANEOUS STREAMFLOW

Figure 27. Daily and instantaneous streamflow at the time of sample collection, and the interquartile range of mean daily streamflows for the period of record, and percentage of time streamflows are equaled or exceeded at the upper Green River (site 10) in the Puget Sound Basin study unit, Washington.

Green-Duwamish River Basin Water Quality

Forty-two water samples from site 6 (table 14), 37 samples from site 7 (table 15), 36 samples from site 8 (table 16) and site 9 (table 17), and 24 samples from site 10 (table 18) were collected for the analysis of physical properties, field parameters, and concentrations of inorganic constituents, organic carbon, and suspended sediment. At site 6, 24 samples were collected for pesticide and VOC analyses; at site 7, 2 samples collected during a storm were analyzed for pesticides and VOCs. With some exceptions, particularly at sites 6 and 7, most applicable standards and criteria for drinking water, ambient water quality for beneficial uses, and the protection of aquatic life were met by the water quality at the sites in this basin. In samples from sites 6 and 7, iron and manganese concentrations often exceeded USEPA SMCLs for drinking water.

High-quality water from headwaters in the mountains is the basis of the dilute water chemistry observed in samples from the mainstem Green and Duwamish Rivers. The chemically dilute nature of the water quality was indicated by the conductivity and dissolved-solids concentrations. As the river flows from site 10 on the upper Green downstream to site 6. there was an increasing trend in major-ion and nutrient concentrations, as indicated by the medians (fig. 28). In samples from site 6, median conductivity and dissolved-solids concentration were 87 µS/cm and 62 mg/L, respectively (table 14), and from site 10, median conductivity and dissolved-solids concentration were 41 µS/cm and 36 mg/L, respectively (table 18). On the basis of median concentrations, calcium and bicarbonate were the dominant cation and anion, respectively, making up the dissolved solids at sites 6 and 10 (fig. 28). Nutrient concentrations were moderately low at site 6, with at least 10 percent of organic nitrogen and phosphorus values below laboratory MRLs. However, 25 percent of the total phosphorus concentrations were greater than 0.1 mg/L, USEPA's (1986a) desired goal to prevent nuisance plant growth in streams (table 14). At site 10, most organic-nitrogen concentrations and half of the total and dissolved phosphorus concentrations were below laboratory MRLs (table 18).

Concentrations of water-chemistry constituents were higher at sites 7, 8, and 9 on lowland tributaries to the Green-Duwamish than in the mainstem river. The constituent concentrations at these sites ranged from moderately high at site 7 to moderately low at sites 8 and 9. At site 7, the median conductivity was 242 μ S/cm and the median dissolved-solids concentration was 152 mg/L (table 15). At sites 8 and 9, median conductivities were less than 150 µS/cm and median dissolved-solids concentrations were less than 110 mg/L (tables 16 and 17). On the basis of median concentrations at site 7, the dominant anion was bicarbonate; the cations were a mix of sodium, calcium, and magnesium in nearly equal proportions (fig. 28). At sites 8 and 9, the dominant cation was calcium and the dominant anion was bicarbonate.

Nutrient concentrations were moderately high in samples from sites 7 and 9, with more than 75 percent of the values for organic nitrogen and phosphorus above laboratory MRLs. In addition, at least 50 percent of the total phosphorus concentrations at both of these sites were greater than 0.1 mg/L, USEPA's (1986a) desired goal to prevent nuisance plant growth in streams. Nutrient concentrations at site 8 were moderately low, with at least 10 percent of organicnitrogen and phosphorus concentrations below laboratory MRLs. Ground-water discharge and human agricultural and urban land-use activities are the likely sources of chemical constituents that contribute to the more concentrated water chemistry in the tributaries.

In addition to monthly routine samples, from 17 to 36 percent of the samples collected at each of the five sites were targeted to stormflow events. The highest concentrations of nitrogen, phosphorus, and suspended sediment tended to occur in samples collected on the rising limb or near the peak of the hydrograph during runoff events (figs. 29, 30, 31, 32, and 33). Kendall's τ , which ranged from 0.4 to 0.6 (table 19), indicated that concentrations of suspended organic carbon and suspended sediment varied directly with streamflows at the five sites in this basin. Concentrations of dissolved solids and major ions, such as bicarbonate, varied inversely with streamflow $(\tau = -0.6 \text{ to } -0.8)$, except at site 9 and site 10. Although there was a general tendency for dissolved-solids concentrations to vary inversely with streamflow at these two sites, τ was only -0.1 and -0.2, respectively.

Seasonality in water quality is defined by the long-term hydrographs for all the sites except Springbrook Creek (site 7). The high-flow period is typically from October to February for sites 6 and 10 and from November to February for sites 8 and 9. The transition period, from March to July at sites 6 and 10, is also a period of relatively high flows because of spring snowmelt or releases of water from Howard A. Hanson Dam; but at sites 8 and 9, the transition period is from March to June and features diminishing flows as summer approaches. The low-flow period is August and September for sites 6 and 10 and from July to September at sites 8 and 9. Seasonality in Springbrook (site 7) was defined to be the same as for the other two tributaries, Big Soos and Newaukum (sites 8 and 9). Except at sites 7 and 9, the highest nutrient and suspended-sediment concentrations typically occurred in samples collected during the high-flow period (figs. 29, 31, and 33). At sites 7 and 9, some of the highest nutrient and suspended-sediment concentrations were observed in samples collected during the transition period (figs. 30 and 32).

Site 6: The water in the Duwamish was of generally good quality except at times when iron and manganese concentrations were relatively large and a number of pesticides and VOCs were present. Ten percent of the samples had iron and manganese concentrations greater than 400 and 70 μ g/L, which exceeded USEPA SMCLs of 300 and 50 µg/L, respectively, for drinking water (see table 2). These exceedances occurred mostly in late spring or summer (July and August, 1996) when streamflows were about $500 \text{ ft}^3/\text{s}$ or less. All nitrogen species analyzed for were present in most samples, however nitrate, with a median concentration of 0.41 mg/L, and total organic nitrogen, with a median of 0.2 mg/L (estimated by logprobability regression), were the dominant nitrogen species (fig. 28).

Site 7: The water in Springbrook was of fair quality; concentrations of iron and manganese were frequently high and instantaneous dissolved-oxygen concentrations low. More than half of the samples, with concentrations greater than 500 μ g/L, exceeded USEPA drinking-water SMCL for iron, and 90 percent of the samples, with concentrations greater than 70 μ g/L, exceeded USEPA drinking-water SMCL for manganese. In 25 of the 37 samples, the concentration of dissolved oxygen measured at the time of sample collection did not meet the Washington State standard of 8.0 mg/L minimum concentration for a Class A water body (see <u>table 2</u>). On two occasions, the water temperature at the time of sample collection was 18.1°C and exceeded the Washington State standard of 18.0°C maximum temperature for a Class A water body. All nitrogen species analyzed for were present above laboratory MRLs in nearly all the samples. The dominant nitrogen species were total and dissolved organic nitrogen with median concentrations of 0.66 and 0.44 mg/L, respectively, and nitrate with a median of 0.43 mg/L (fig. 28).

Contrary to the other four sites in the basin, constituent concentrations in Springbrook tended to vary inversely with streamflow, indicating dilution effects from rain and occasionally from snowmelt. Kendall's τ for the nitrogen species, orthophosphate, bicarbonate, iron, manganese, conductivity, and dissolved solids ranged from -0.1 to -0.8 (table 19). These tendencies, in addition to the relatively high nitrogen and phosphorus concentrations during the transition and low-flow periods (fig. 30), suggest that ground water is an important source of nutrients at this site. Other factors suggesting an important groundwater contribution to the quality of water included reddish precipitates on undisturbed bottom sediments, low dissolved-oxygen concentrations, and the yearround high concentrations of iron and manganese in many of the samples. Dissolved-oxygen concentrations generally did not meet the State's standard for a Class A water body except during the winter months of November, December, and January.

Site 8: The water in Big Soos was of good quality. At all times during the study, water temperatures, dissolved-oxygen concentrations, and pH levels met Washington State standards for a Class A water body. However, samples collected from April 1997-September 1997 showed E. coli to be present in the creek. Concentrations of E. coli ranged from 21 to 750 col/100 mLs (table 33). Of the eight samples collected for bacteria analyses, two samples exceeded 298 col/100 mLs, USEPA's (1986b) recommended single-sample level for moderate, full-body contact recreation. Otherwise, all other applicable standards and criteria for drinking water, ambient water quality for beneficial uses, or the protection of aquatic life were met by the water quality at this site. Nitrate, with a median concentration of 0.88 mg/L, was the dominant nitrogen species (fig. 28). Dissolved and total organic nitrogen was present in many of the samples, but median concentrations were less than about 0.2 mg/L.

Site 9: Water in Newaukum Creek was of moderately good quality in the respect that water temperatures, dissolved-oxygen concentrations, and pH levels met Washington State standards for a Class A water body. However, nutrient concentrations were large, with a maximum nitrate concentration of 3.5 mg/L, ammonia of 1.3 mg/L, and total phosphorus of 0.66 mg/L. Nitrate, with a median concentration of 2.1 mg/L, was the dominant nitrogen species (fig. 28). On one occasion, a water sample had an iron concentration of 310 µg/L that exceeded USEPA SMCL for drinking water. In a sample collected on August 4, 1998, concentrations of fecal-coliform bacteria exceeded the State's standard of 100 col/100 mLs for a Class A water body and enterococci bacteria exceeded 89 col/100 mLs. USEPA's (1986b) recommended single-sample level for moderate, full-body contact recreation (table 33).

Site 10: Excluding a single sample that was collected during a large runoff event in October 1997, the water in the upper Green River was of high quality, similar to that of the study's reference site on the NF Skokomish R. Organic nitrogen was detected only in the October storm sample. Nitrate, detected in only 38 percent of the samples, had a median concentration of 0.04 mg/L (estimated by log-probability regression) (fig. 28). In samples collected from April 1997-October 1997, E. coli were present at low concentrations, ranging from less than 1 to 10 col/100 mLs (table 33). None of the eight samples collected for bacteria analyses exceeded USEPA's (1986b) recommended single-sample levels for contact recreation. In the October storm sample, the suspended-sediment concentration was 243 mg/L and was the maximum observed for this site; however, 90 percent of sample concentrations were less than 15 mg/L. Also in this storm sample, the iron concentration of 520 µg/L was the maximum observed at this site and exceeded the USEPA SMCL for drinking water. All other applicable standards and criteria for drinking water, ambient water quality for beneficial uses, and protection of aquatic life were met by the water quality at this site.

Table 14. Summary of values of field measurements and concentrations of nutrients, major ions, organic carbon, and suspended sediment in samples from Duwamish River (site 6) in the Puget Sound Basin study unit, Washington

[Measurement or concentration - Percentile: Percentiles for data sets with 10 percent or more censored data (values less than the MRL) are estimated by log-probability regression (Helsel and Cohn, 1988). Concentrations are dissolved and in milligrams per liter unless otherwise specified. Abbreviations: MRL, minimum reporting level; µS/cm, microsiemens per centimeter at 25 degrees Celsius; CaCO₃, calcium carbonate; <, less than; µg/L, micrograms per liter]

				Measur	ement or co	ncentratior	1		
				Percentile					Number of
Constituent or property	Mini- mum	10	25	50 (Median)	75	90	Maxi- mum	Number of samples	samples below MRL (see <u>tables</u> <u>A1-A3</u>)
Water temperature (degrees Celsius)	4.1	5.75	6.8	9.05	13.5	17.6	19.1	42	0
Specific electrical conductance, (µS/cm)	47	49	64	87	102	169	187	42	0
pH (units)	7.0	7.2	7.4	7.4	7.5	7.6	7.7	42	0
Dissolved oxygen	7.6	8.2	9.3	10.25	11.35	11.9	12.4	42	0
Ammonia nitrogen	< 0.015	< 0.015	0.02	0.03	0.05	0.09	0.12	42	11
Ammonia-plus-organic nitrogen	<.1	<.1	<.1	.12	.18	.29	.4	42	31
Ammonia-plus-organic nitrogen, total	<.1	<.1	.13	.2	.4	.57	1.5	42	15
Nitrite nitrogen	<.01	<.01	<.01	.006	.01	.02	.03	42	26
Nitrite-plus-nitrate nitrogen	.08	.21	.3	.41	.46	.63	.82	42	0
Phosphorus, total	.02	.03	.03	.05	.11	.17	.73	42	0
Phosphorus	<.01	<.01	<.01	.02	.03	.05	.07	42	16
Orthophosphate phosphorus	<.01	<.1	.011	.02	.03	.05	.06	42	4
Alkalinity (as CaCO ₃)	14	18	23.5	31	39	55	64	42	0
Bicarbonate (as CaCO ₃)	17	22	28.5	37.5	47	66	77	42	0
Calcium	4.1	4.7	6.2	7.8	8.95	13	14	41	0
Magnesium	1.2	1.3	1.6	2.3	2.9	4.5	5.1	41	0
Sodium	2.6	2.8	3.4	5.0	6.6	12.8	14	41	0
Potassium	.3	.5	.7	.84	1.1	1.3	1.6	41	0
Chloride	1.3	1.6	2.0	3.4	5.7	12.8	15	41	0
Sulfate	1.8	2.7	3.2	3.7	4.6	5.3	6.1	41	0
Fluoride	<.1	<.1	<.1	<.1	<.1	<.1	<.1	41	41
Silica	9.3	11	12	14	14	16	18	41	0
Iron, in μg/L	32	50	76	130	195	427	540	41	0
Manganese, in µg/L	6	11	16	28	48	77	110	41	0
Dissolved solids, residue at 180 degrees Celsius	36	42	4.57	62	72	102	120	41	0
Organic carbon	1.3	1.4	1.6	1.95	2.5	3.5	4.5	42	0
Organic carbon, suspended	.2	.3	.4	.6	1.0	2.4	12	42	0
Sediment, suspended	7	9	15	31	109	250	787	41	0

 Table 15.
 Summary of values of field measurements and concentrations of nutrients, major ions, organic carbon, and suspended sediment in samples from Springbrook Creek (site 7) in the Puget Sound Basin study unit, Washington

[Measurement or concentration - Percentile: Percentiles for data sets with 10 percent or more censored data (values less than the MRL) are estimated by log-probability regression (Helsel and Cohn, 1988). Concentrations are dissolved and in milligrams per liter unless otherwise specified. Abbreviations: MRL, minimum reporting level; µS/cm, microsiemens per centimeter at 25 degrees Celsius; CaCO₃, calcium carbonate; <, less than; µg/L, micrograms per liter]

				Meas	urement or co	ncentration			
-				Percentile					Number of
Constituent or property	Mini- mum	10	25	50 (Median)	75	90	Maxi- mum	Number of samples	samples below MRL (see <u>tables</u> <u>A1-A3</u>)
Water temperature (degrees Celsius)	1.3	5.2	7.7	10.1	16.3	17.1	18.1	37	0
Specific electrical conductance, (µS/cm)	63	86	147.5	242	329	413	551	37	0
pH (units)	6.9	7.0	7.1	7.2	7.3	7.4	7.6	37	0
Dissolved oxygen	2.3	2.5	4.15	5.6	8.85	10.1	12.2	37	0
Ammonia nitrogen	< 0.02	0.02	0.09	0.2	0.36	0.5	0.68	37	3
Ammonia-plus-organic nitrogen	.25	.3	.36	.44	.66	.9	1.0	37	0
Ammonia-plus-organic nitrogen, total	.3	.44	.51	.66	.77	.92	1.2	37	0
Nitrite nitrogen	<.01	.007	.01	.02	.03	.04	.06	37	9
Nitrite-plus-nitrate nitrogen	.21	.3	.32	.43	.52	.67	.75	37	0
Phosphorus, total	.078	.09	.11	.17	.21	.25	.38	37	0
Phosphorus	<.01	.01	.02	.03	.045	.06	.08	37	3
Orthophosphate phosphorus	<.01	.01	.02	.03	.04	.07	.08	37	1
Alkalinity (as CaCO ₃)	19	29	47	89	132	159	174	37	0
Bicarbonate (as CaCO ₃)	24	35	57	109	161	194	212	37	0
Calcium	5.4	7.5	11	17	24	27	28	37	0
Magnesium	1.9	2.7	4.25	7.3	12	14	16	37	0
Sodium	3.2	4.3	8.2	17	26	35	58	37	0
Potassium	1.3	1.5	1.9	2.85	3.9	4.4	6.0	37	0
Chloride	3.2	3.8	6.4	14	20	26	54	37	0
Sulfate	3.6	4.5	7.2	9.5	11	12	12	37	0
Fluoride	<.1	<.1	.1	.16	.2	.3	.6	37	8
Silica	5.0	6.7	10	18	26	31	33	37	0
Iron, in μg/L	79	204	253	510	1,070	1,600	1,940	37	0
Manganese, in µg/L	47	71	128	230	467	590	964	37	0
Dissolved solids, residue at 180 degrees Celsius	42	56	90	152	220	249	321	37	0
Organic carbon	2.9	3.4	4.65	5.3	6.1	6.5	6.7	37	0
Organic carbon, suspended	.2	.3	.5	.8	2.0	3.5	9.1	37	0
Sediment, suspended	5	8	12	17	55	81	215	35	0

 Table 16.
 Summary of values of field measurements and concentrations of nutrients, major ions, organic carbon, and suspended sediment in samples from Big Soos Creek (site 8) in the Puget Sound Basin study unit, Washington

Measurement or concentration - Percentile: Percentiles for data sets with 10 percent or more censored data (values less than the MRL) are estimated by logprobability regression (Helsel and Cohn, 1988). Concentrations are dissolved and in milligrams per liter unless otherwise specified. **Abbreviations:** [MRL, minimum reporting level; µS/cm, microsiemens per centimeter at 25 degrees Celsius; CaCO₃, calcium carbonate; <, less than; µg/L, micrograms per liter]

	Measurement or concentration										
				Percentile					Number of		
Constituent or property	Mini- mum	10	25	50 (Median)	75	90	Maxi- mum	Number of samples	samples below MRL (see <u>tables</u> <u>A1-A3</u>)		
Water temperature (degrees Celsius)	5.1	6.1	7.1	9.7	12.9	14.9	16.3	37	0		
Specific electrical conductance, (µS/cm)	87	102	110.5	123	134	141	147	37	0		
pH (units)	7.3	7.6	7.7	7.8	7.9	8.1	8.1	37	0		
Dissolved oxygen	9.7	9.9	10.4	11.3	12.15	12.6	12.9	36	0		
Ammonia nitrogen	< 0.015	< 0.015	< 0.015	0.011	0.03	0.06	0.18	36	21		
Ammonia-plus-organic nitrogen	<.1	.09	.13	.17	.3	.33	.6	36	16		
Ammonia-plus-organic nitrogen, total	<.2	<.2	<.2	.225	.4	.56	.99	36	11		
Nitrite nitrogen	<.01	<.01	<.01	.01	.02	.03	.05	36	20		
Nitrite-plus-nitrate nitrogen	.482	.64	.68	.875	.98	1.1	2.6	36	0		
Phosphorus, total	<.01	.01	.02	.03	.04	.13	.33	36	4		
Phosphorus	<.01	<.01	.01	.014	.02	.03	.16	36	17		
Orthophosphate phosphorus	<.01	.01	.01	.02	.02	.03	.17	36	6		
Alkalinity (as CaCO ₃)	23	31	34	40	47	50	54	35	0		
Bicarbonate (as CaCO ₃)	28	38	41	49	57	61	65	35	0		
Calcium	7	8.6	9.5	11	12	13	14	36	0		
Magnesium	2.4	3.2	3.4	3.8	4.4	4.8	5	36	0		
Sodium	4.1	4.9	5.4	5.8	6.3	6.6	6.9	36	0		
Potassium	.9	.93	1.1	1.2	1.4	1.6	2.1	36	0		
Chloride	.81	2.8	3.0	3.4	3.8	4.1	4.9	36	0		
Sulfate	4.8	6.6	7.5	8.4	9.3	9.9	13	36	0		
Fluoride	<.1	<.1	<.1	<.1	<.1	<.1	.1	36	34		
Silica	8.3	11	12	14	16	18	19	36	0		
Iron, in µg/L	38	47	56	74	95	112	150	36	0		
Manganese, in µg/L	4	5.7	8.0	9	12	14	15	36	0		
Dissolved solids, residue at 180 degrees Celsius	58	69	77	84	90	95.5	102	36	0		
Organic carbon	1.3	1.6	2.7	3.8	5.1	5.7	7.3	35	0		
Organic carbon, suspended	<.1	.2	.3	.4	.7	1.3	5.6	34	2		
Sediment, suspended	<1	1	5	8	31	121	292	35	3		

 Table 17.
 Summary of values of field measurements and concentrations of nutrients, major ions, organic carbon, and suspended sediment in samples from Newaukum Creek (site 9) in the Puget Sound Basin study unit, Washington

[Measurement or concentration - Percentile: Percentiles for data sets with 10 percent or more censored data (values less than the MRL) are estimated by log-probability regression (Helsel and Cohn, 1988). Concentrations are dissolved and in milligrams per liter unless otherwise specified. Abbreviations: MRL, minimum reporting level; µS/cm, microsiemens per centimeter at 25 degrees Celsius; CaCO₃, calcium carbonate; <, less than; µg/L, micrograms per liter]

				Measur	ement or co	ncentration	1		
-				Percentile					Number of
Constituent or property	Mini- mum	10	25	50 (Median)	75	90	Maxi- mum	Number of samples	samples below MRL (see <u>tables</u> <u>A1-A3</u>)
Water temperature (degrees Celsius)	5.5	5.8	6.4	8.7	11.95	15.3	17.3	36	0
Specific electrical conductance (µS/cm)	97	127.5	136.5	148	155	161	175	36	0
pH (units)	7.6	7.8	7.9	8.0	8.0	8.1	8.2	36	0
Dissolved oxygen	8.7	9.7	10.65	11.35	12.2	12.8	13.1	36	0
Ammonia nitrogen	< 0.015	< 0.015	0.014	0.052	0.19	0.32	1.3	36	9
Ammonia-plus-organic nitrogen	<.2	<.2	.2	.4	.9	1.1	2.6	36	9
Ammonia-plus-organic nitrogen, total	<.2	<.2	.22	.525	1.0	1.6	2.3	36	6
Nitrite nitrogen	<.01	.01	.02	.03	.05	.06	0.07	36	2
Nitrite-plus-nitrate nitrogen	1.0	1.5	1.7	2.1	2.4	2.9	3.5	36	0
Phosphorus, total	.02	.04	.06	.16	.34	.46	.66	36	0
Phosphorus	<.01	.037	.06	.1	.275	.37	.51	36	2
Orthophosphate phosphorus	<.01	.05	.06	.1	.22	.31	.38	36	1
Alkalinity (as CaCO ₃)	26	35	41	48	53	55	61	35	0
Bicarbonate (as CaCO ₃)	32	43	50	59	64	67	75	35	0
Calcium	7.7	10	12	13	15	16	17	36	0
Magnesium	2.4	3.3	3.8	4.2	4.6	4.9	5.2	36	0
Sodium	4.3	5.4	5.9	6.2	6.6	7.5	7.8	36	0
Potassium	1.5	1.7	2.3	3.4	5.3	6.4	7.7	36	0
Chloride	.9	4.3	4.5	5	6.2	7.1	8.9	36	0
Sulfate	3.8	5.1	5.6	6.0	7.3	8.6	14	36	0
Fluoride	<.1	<.1	<.1	<.1	<.1	<.1	.1	36	35
Silica	11	13	16	18	20	20	21	36	0
Iron, in μg/L	15	26	50	97	140	207	330	36	0
Manganese, in µg/L	<2	2.0	3.3	5.2	9.0	13	20	36	2
Dissolved solids, residue at 180 degrees Celsius	70	94	96	107	113	118	125	36	0
Organic carbon	1.2	1.5	2.7	4.2	8.1	9.4	11	35	0
Organic carbon, suspended	.2	.3	.4	.7	1.3	1.9	3.9	35	0
Sediment, suspended	<1	2	5	9.5	19	62	123	34	1

 Table 18.
 Summary of values of field measurements and concentrations of nutrients, major ions, organic carbon, and suspended sediment in samples from the upper Green River (site 10) in the Puget Sound Basin study unit, Washington

[Measurement or concentration - Percentile: Percentiles for data sets with 10 percent or more censored data (values less than the MRL) are estimated by log-probability regression (Helsel and Cohn, 1988). Concentrations are dissolved and in milligrams per liter unless otherwise specified. Abbreviations: MRL, minimum reporting level; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; CaCO₃, calcium carbonate; <, less than; μ g/L, micrograms per liter]

				Measur	ement or co	ncentratio	ı		
				Percentile					Number of
Constituent or property	Mini- mum	10	25	50 (Median)	75	90	Maxi- mum	Number of samples	samples below MRL (see <u>tables</u> <u>A1-A3</u>)
Water temperature (degrees Celsius)	3.2	3.7	4.95	6.5	9.35	12.6	13.1	25	0
Specific electrical conductance (µS/cm)	33	33	36	41	48	51	53	25	0
pH (units)	7.3	7.3	7.5	7.6	7.7	7.8	7.8	24	0
Dissolved oxygen	9.4	9.6	10.9	11.95	13.6	14.15	15	24	0
Ammonia nitrogen	< 0.015	< 0.015	< 0.015	0.012	0.02	0.05	0.07	24	14
Ammonia-plus-organic nitrogen	<.1	<.1	<.1	<.1	<.1	<.1	<.1	24	24
Ammonia-plus-organic nitrogen, total	<.1	<.1	<.1	<.1	<.1	<.1	.46	24	23
Nitrite nitrogen	<.01	<.01	<.01	<.01	.01	.02	.02	24	19
Nitrite-plus-nitrate nitrogen	<.05	.02	.03	.04	.07	.09	.13	24	15
Phosphorus, total	<.01	<.01	<.01	<.01	.01	.026	.16	24	18
Phosphorus	<.01	<.01	<.01	<.01	<.01	.014	.03	24	21
Orthophosphate phosphorus	<.01	.006	.008	.01	.018	.02	.02	24	9
Alkalinity (as CaCO ₃)	13	14.5	16	18	22	23	24	24	0
Bicarbonate (as CaCO ₃)	16	18	19.5	22	27	28	29	24	0
Calcium	3.3	3.5	3.7	4.4	5.1	5.7	5.9	24	0
Magnesium	.56	.58	.665	.75	.88	.96	1.0	24	0
Sodium	2.2	2.3	2.6	2.9	3.3	3.45	3.7	24	0
Potassium	<.1	.1	.1	.125	.2	.225	.49	24	1
Chloride	.4	.5	.53	.7	.79	1.1	1.2	24	0
Sulfate	.63	.71	.9	1.03	1.27	1.3	1.5	24	0
Fluoride	<.1	<.1	<.1	<.1	<.1	<.1	<.1	24	24
Silica	11	12	13	13	13	13	15	24	0
Iron, in μg/L	<3	<3	3.0	4.0	9.8	29	520	24	5
Manganese, in µg/L	<1	<1	<1	<1	<1	<1	8	24	22
Dissolved solids, residue at 180 degrees Celsius	23	27	33	36	38	40	43	24	0
Organic carbon	.5	.6	.6	.9	1.4	2.5	4.7	23	0
Organic carbon, suspended	<.1	<.1	.1	.11	.2	.45	3.1	24	7
Sediment, suspended	<1	<1	1	1	2	15	243	22	4

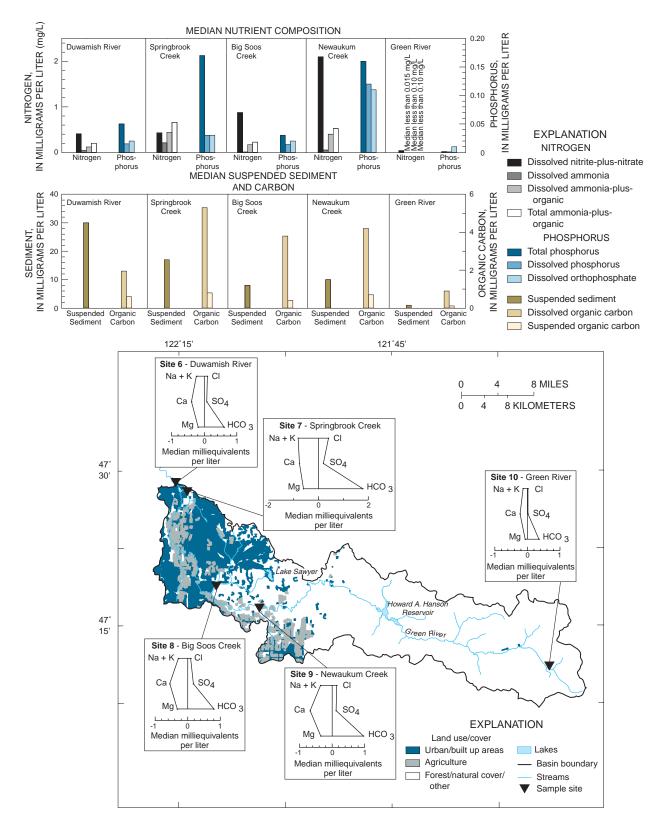


Figure 28. Median concentrations of nutrients, suspended sediment, organic carbon, and major ions in samples from the Duwamish River (site 6), Springbrook Creek (site 7), Big Soos Creek (site 8), Newaukum Creek (site 9), and the upper Green River (site 10) in the Puget Sound Basin study unit, Washington.

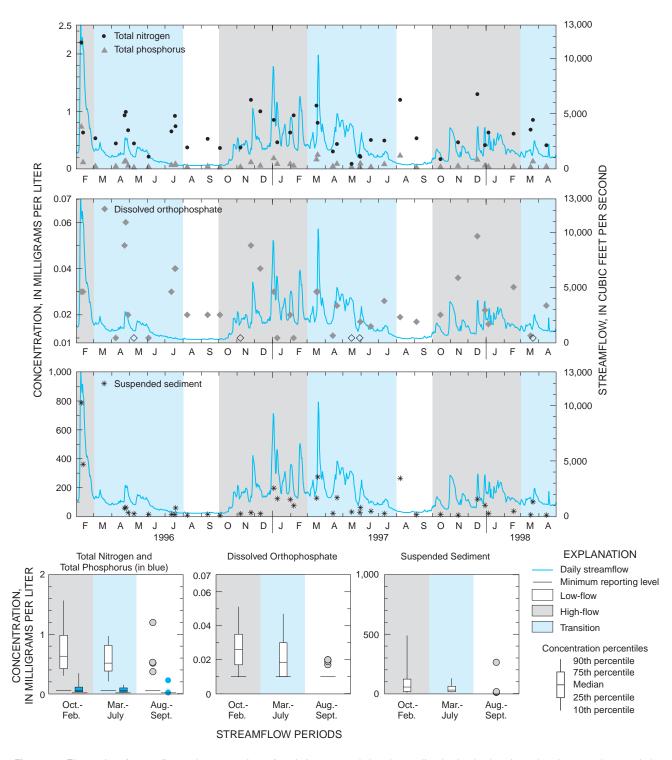


Figure 29. Time series of streamflow and concentrations of total nitrogen, total phosphorus, dissolved orthophosphate phosphorus, and suspended sediment in samples, and concentrations by three streamflow periods, for the Duwamish River (site 6) in the Puget Sound Basin study unit, Washington.

(Truncated boxplots of concentration percentiles require a minimum of nine observations, otherwise concentrations are plotted as individual points. Censored data in the time-series graphs are shown as an open symbol. Boxplots are truncated at the minimum reporting level indicated by solid line.)

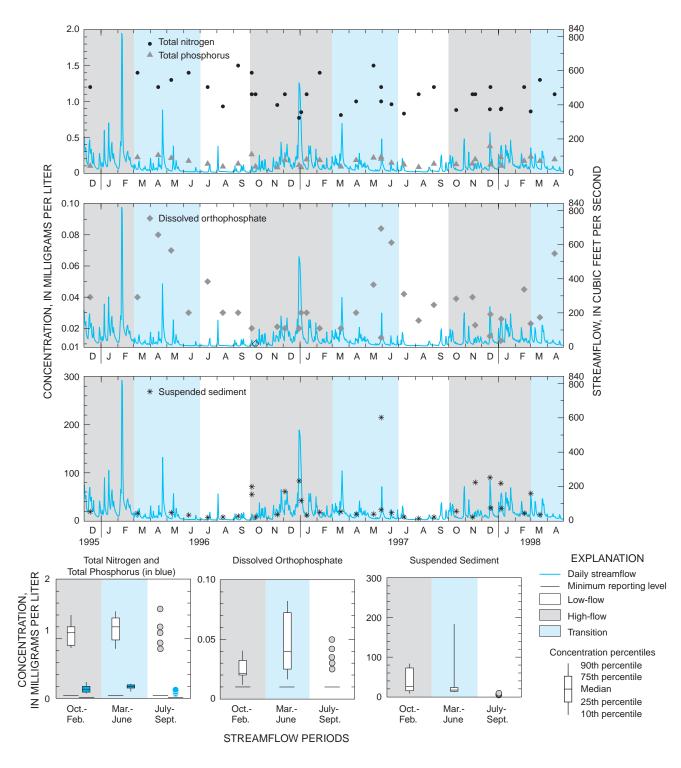


Figure 30. Time series of streamflow and concentrations of total nitrogen, total phosphorus, dissolved orthophosphate phosphorus, and suspended sediment in samples, and concentrations by three streamflow periods, for Springbrook Creek (site 7) in the Puget Sound Basin study unit, Washington.

(Truncated boxplots of concentration percentiles require a minimum of nine observations, otherwise concentrations are plotted as individual points. Censored data in the time-series graphs are shown as an open symbol. Boxplots are truncated at the minimum reporting level indicated by solid line.)

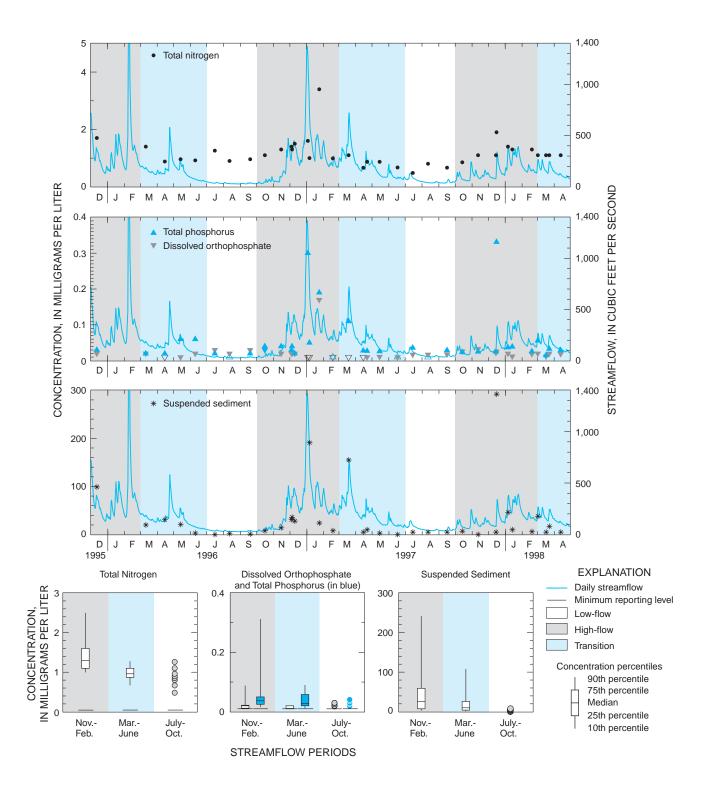


Figure 31. Time series of streamflow and concentrations of total nitrogen, total phosphorus, dissolved orthophosphate phosphorus, and suspended sediment in samples, and concentrations by three streamflow periods, for Big Soos Creek (site 8) in the Puget Sound Basin study unit, Washington.

(Truncated boxplots of concentration percentiles require a minimum of nine observations, otherwise concentrations are plotted as individual points. Censored data in the time-series graphs are shown as an open symbol. Boxplots are truncated at the minimum reporting level indicated by solid line.)

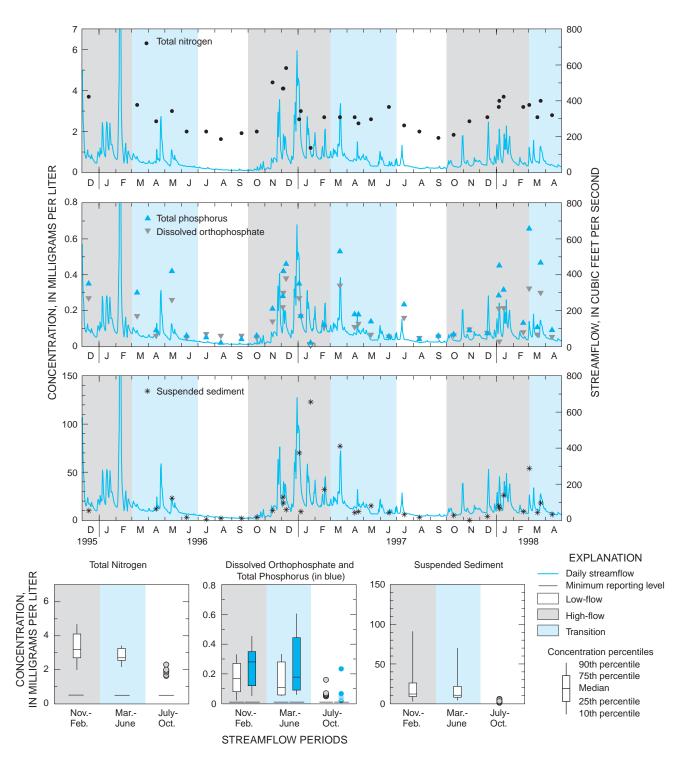


Figure 32. Time series of streamflow and concentrations of total nitrogen, total phosphorus, dissolved orthophosphate phosphorus, and suspended sediment in samples, and concentrations by three streamflow periods, for Newaukum Creek (site 9) in the Puget Sound Basin study unit, Washington.

(Truncated boxplots of concentration percentiles require a minimum of nine observations, otherwise concentrations are plotted as individual points. Censored data in the time-series graphs are shown as an open symbol. Boxplots are truncated at the minimum reporting level indicated by solid line.)

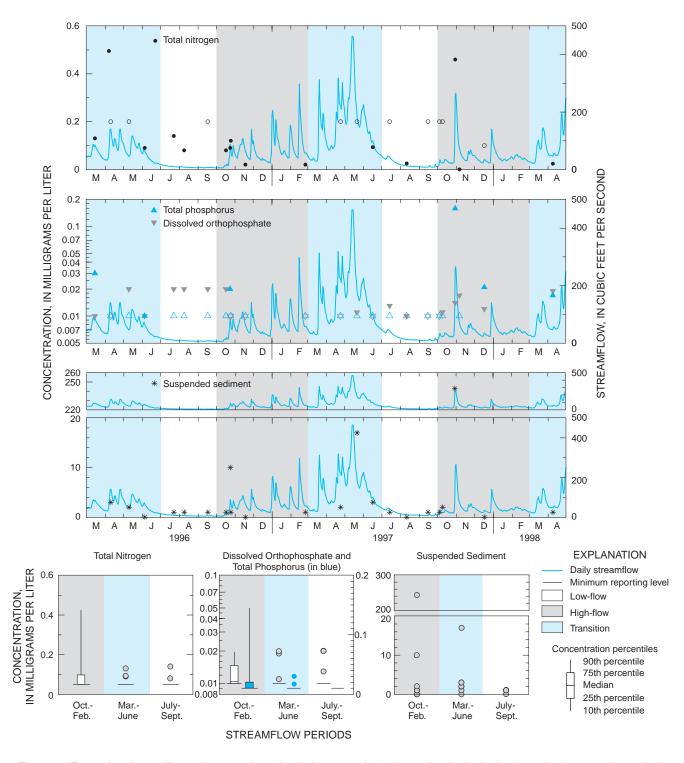


Figure 33. Time series of streamflow and concentrations of total nitrogen, total phosphorus, dissolved orthophosphate phosphorus, and suspended sediment in samples, and concentrations by three streamflow periods, for the upper Green River (site 10) in the Puget Sound Basin study unit, Washington.

(Truncated boxplots of concentration percentiles require a minimum of nine observations, otherwise concentrations are plotted as individual points. Censored data in the time-series graphs are shown as an open symbol. Boxplots are truncated at the minimum reporting level indicated by solid line.) **Table 19**.Correlation between selected water-quality characteristics or chemical constituents and streamflow for the Duwamish River (site 6),Springbrook Creek (site 7), Big Soos Creek (site 8), Newaukum Creek (site 9), and the upper Green River (site 10) in the Puget Sound Basin study unit,Washington

		Kendall	's tau correlation co	pefficient	
Water-quality characteristic or - chemical constituent	Duwamish River (Site 6)	Springbrook Creek (Site 7)	Big Soos Creek (Site 8)	Newaukum Creek (Site 9)	Upper Green River (Site 10)
Specific electrical conductance	-0.73	-0.77	-0.80	-0.53	-0.64
Dissolved solids	70	77	60	12	21
Total nitrogen	.15	35	40	.47	.16
Dissolved nitrite-plus-nitrate nitrogen	.10	20	.2	.08	.08
Total ammonia-plus-organic nitrogen	.24	20	.50	.66	.07
Dissolved ammonia-plus-organic nitrogen	.12	45	.30	.62	<.01
Total phosphorus	.36	.12	.41	.64	.18
Dissolved orthophosphate phosphorus	.08	27	18	.54	30
Dissolved organic carbon	.34	33	.62	.59	.19
Suspended organic carbon	.37	.42	.48	.59	.54
Suspended sediment	.57	.61	.65	.64	.35
Bicarbonate	75	76	78	77	72
Iron	51	25	.27	.45	.26
Manganese	60	47	35	.50	.08

Duwamish River Organic Chemistry

Thirteen pesticides, mostly herbicides, were found in Duwamish River (site 6) samples collected from March 1996 through May 1997 (table 20). The herbicide simazine was detected most frequently, found in 18 of 24 samples at concentrations as high as $0.194 \mu g/L$ and with a median of $0.0195 \mu g/L$. The herbicide prometon, present in 15 samples, was the next most frequently detected pesticide and was closely followed in frequency by detections of the herbicides atrazine and tebuthiuron, which were present in 14 samples. These herbicides were also detected in a large percentage of samples from study units nationwide (Larson and others, 1997), although in the Duwamish, tebuthiuron was detected more frequently, occurring in about 60 percent of samples compared to the national rate of about 10 percent of samples. Diazinon in eight samples and propargite in one sample were the only insecticides detected. Diazinon concentrations in two samples exceeded 0.04 μ g/L, a limit recommended for the protection of aquatic life by Menconi and Cox (1994). No other pesticide concentration exceeded water-quality criteria concentrations established for drinking water or aquatic life. Most concentrations of the frequently detected pesticides at site 6 ranked within or below the middle 50 percent range of concentrations in mixed land-use river basins studied nationwide in 36 NAWQA study units during 1991–98. The exceptions were a few samples having simazine, tebuthiuron, and diazinon concentrations in the highest 25 percent range (Ebbert and others, 2000).

All but two (2,4-D and metolachlor) of the pesticides detected in samples from this basinintegrator site were found in samples from Thornton Creek (site 11), the study's only intensively sampled urban-indicator stream, but one that is not a tributary to the Green-Duwamish River. Metolachlor was detected, however, in samples collected during a storm event from Springbrook (site 7), a tributary to the Duwamish (table 34 at the end of the report). Although known more for its use as an agricultural herbicide in other parts of the country, metolachlor has also been indicated for use on turf and fencelines, and on golf courses in the northeast United States (Jack Barbash, U.S. Geological Survey, written commun., December 1998) (see <u>table 27</u>). In the late 1980's, it was estimated that about 5,300 pounds of metolachlor were applied in King County for agricultural and nonagricultural purposes (Tetra Tech, 1988).

Although several pesticides tended to be detected more during the rainy season from November to April (fig. 34), concentrations did not correlate with streamflow (τ less than 0.3; p-values less than 0.05). Season, timing of applications, and storm events appeared to have the most influence on pesticide detection frequencies and concentrations. Highest concentrations for most pesticides tended to occur in spring samples, particularly in storm-event samples. Diazinon concentrations tended to be highest in spring samples, corresponding to the season of high application rates (fig. 34). The two times when diazinon concentrations exceeded a recommended level for the protection of aquatic life were in April 1996 storm-event samples. For atrazine, deethylatrazine, prometon, and diuron, the highest concentrations were also observed in the April 1996 storm-event sample.

Of the 86 VOCs that were analyzed for, 26 different compounds were detected in samples from site 6 (table 21). However, only 2 of the 26 compounds (methylbenzene and 1,3-plus-1,4-dimethylbenzene) were detected at concentrations above the 1999 LRLs. Methylbenzene, the most frequently detected compound, was in 16 samples, 59 percent of which had concentrations above the LRL. Chloromethane was detected second-most frequently with 13 detections, but with all of them in concentrations below the LRL. The compound *cis*-1,2-dichloroethene was present in 11 samples, none of which had concentrations above the LRL. The general absence of concentrations above the LRLs could be due in part to dilution, because of the volume of water in this river and because of highquality water released from the upper watershed at Howard A. Hanson Dam. None of the VOC concentrations exceeded any drinking-water or aquaticlife criteria concentrations. Detections or concentrations of methylbenzene and 1,3-plus-1,4dimethylbenzene did not appear to relate with magnitude of streamflow, and although VOCs were found throughout the year at both high streamflow in the winter months and during baseflow conditions, the detections seemed to occur more frequently with rainy wet conditions during winter (fig. 35). Increased methylbenzene concentrations occasionally corresponded to peaks in streamflow such as during the storm in April 1996, but concentrations remained low during other storms such as in January 1997. Similarly, concentrations of 1,3-plus-1,4-dimethylbenzene were generally low throughout the year with occasional increases in concentrations such as during September 1996 and February 1997.

Table 20. Pesticides in water samples from the Duwamish River (site 6) in the Puget Sound Basin study unit, Washington

[Water-quality criteria – Drinking water: U.S. Environmental Protection Agency (1996). Aquatic organisms – Chronic (USGS): U.S. Geological Survey (1999a). Based on 24 samples collected March 1996 to May 1997; all concentrations are in micrograms per liter (µg/L); bold type indicates value above aquatic life criterion; method detection limits are from reports by Zaugg and others (1995), Lindley and others (1996), Werner and others (1996), and U.S. Geological Survey National Water Quality Laboratory Technical Memorandums 98.03A and 96.06A; MCL, maximum contaminant level; HAL, Health advisory level; ^E, Estimated–a qualitative value that is less than the statistically determined method detection limit or lowest calibration standard; –, no value or data]

			Median		Water-quality criteria						
Pesticide	Number of	Maximum concentration	concen-	Method detection	Drinkir	g water	Aquatic	organisms (freshwater)			
	detections	value	tration detected	limit	MCL	HAL	Acute	Chronic	Chronic (USGS)		
Atrazine	14	0.015	0.005	0.001	3	3	¹ 70	¹ 7	1.8		
2,4-D	1	.10	-	.15	70	70	¹ 10	¹ 1	4		
Deethylatrazine	5	^E .005	^E .004	.002	_	_	-	-	-		
Diazinon	8	.083	.011	.002	_	0.6	² 0.16	² 0.04	0.08		
Dichlobenil	3	^E .03	^E .02	^E 1.2	_	_	-	-	-		
Diuron	9	^E .69	.11	.020	_	10	-	-	-		
Metolachlor	12	.013	.004	.002	_	70	-	-	7.8		
Prometon	15	.02	^E .006	.018	_	100	-	-	-		
Pronamide	2	.008	-	.003	_	50	-	-	-		
Propargite	1	.003	_	.013	_	_	_	_	_		
Simazine	18	.194	.0195	.005	4	4	¹ 100	¹ 10	10		
Tebuthiuron	14	.09	.010	.010	-	500	-	-	1.6		
Triclopyr	1	.12	_	.25	_	_	¹ 5,600	¹ 560	_		

¹Norris and Dost (1992).

²Menconi and Cox (1994).

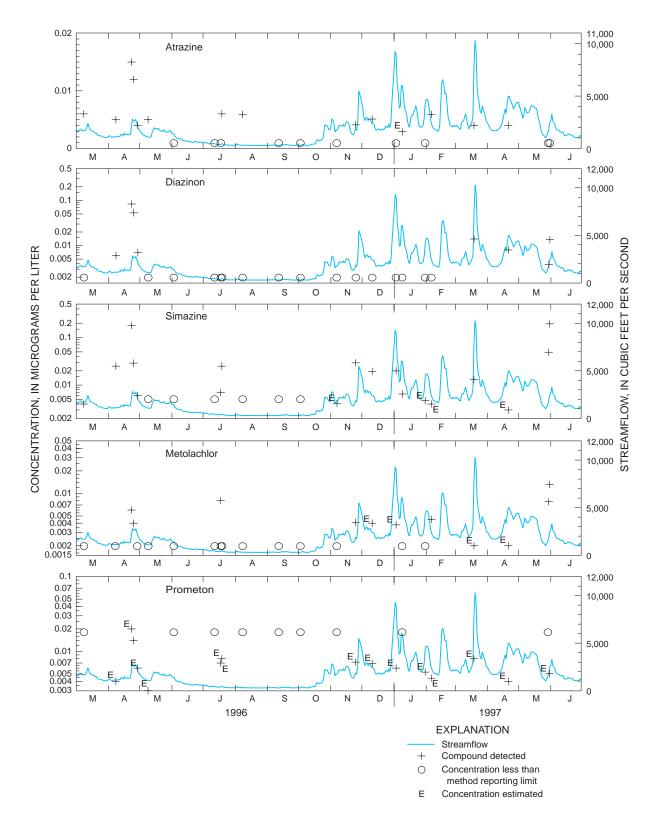


Figure 34. Time series of streamflow and concentrations of selected pesticides detected in samples from the Duwamish River (site 6) in the Puget Sound Basin study unit, Washington.

Table 21. Volatile organic compounds in water samples from the Duwamish River (site 6) in the Puget Sound Basin study unit, Washington

[Water-quality criteria – Drinking water: U.S. Environmental Protection Agency (1996). Based on 24 samples collected between March 1996 to May 1997; all concentrations are in micrograms per liter (µg/L); MRL, method reporting level (Connor and others, 1998); LRL, laboratory reporting level; MCL, maximum contaminant level; HAL, health advisory level; ^E, Estimated–a qualifier for an analytical result based on the long-term method detection level, laboratory reporting level, and lowest calibration standard (Childress and others, 1999); –, no value or data]

						w	ater-quality	criteria
Volatile organic compound	Number of detec- tions	Percentage of detections above 1999 LRL and (number)	Maximum concen- tration value	Median concen- tration detected	MRL (1999 LRL)	Drinkin	ıg water	Aquatic organisms (freshwater)
						MCL	HAL	Chronic
1,1,1-Trichloroethane	2	0	E0.01	-	0.032 (0.032)	200	200	-
1,2,4-Trimethylbenzene	6	0	^E .02	E0.015	.056 (.056)	-	-	_
1,2-Dimethylbenzene (o-Xylene)	5	0	^E .04	E.009	.064 (.06)	10,000	10,000	_
1,3-plus-1,4-Dimethylbenzene (<i>m</i> , <i>p</i> -Xylene)	9	18 (2)	^E .08	^E .01	.064 (.06)	10,000	10,000	-
1,4-Dichlorobenzene	3	0	^E .008	E.003	.05 (.05)	75	75	¹ 26
2-Butanone (Methyl ethyl ketone)	5	0	^E .6	^E .4	1.65 (1.6)	-	_	-
2-Ethyltoluene (o-Ethyl toluene)	1	0	^E .006	_	.1 (.1)	_	_	_
1-Isopropyl-4-methylbenzene (p-Isopropyltoluene)	5	0	^E .006	^E .004	.11 (.11)	-	-	-
4-Methyl-2-pentanone (Methyl isobutyl ketone)	1	0	^E .3	_	.374 (.374)	_	_	-
Acetone	9	0	2.5	^E 1.4	4.904 (5)	_	_	_
Benzene	2	0	^E .09	_	.032 (.1)	5	_	¹ 370
Bromoform	1	0	^E .01	_	.104 (.1)	100	_	_
Carbon disulfide	8	0	^E .06	^E .01	.08 (.37)	_	_	_
Chloroethene (Vinyl chloride)	2	0	^E .01	_	.112 (.11)	2	_	_
Chloromethane (Methyl chloride)	13	0	^E .06	^E .03	.254 (.25)	-	3	_
Dichloromethane (Methylene chloride)	2	0	^E .08	-	.382 (.38)	5	-	¹ 98.1
Ethenylbenzene (Styrene)	2	0	^E .01	_	.042 (.042)	100	100	_
Ethylbenzene	5	0	^E .02	^E .007	.03 (.03)	700	700	¹ 90
Iodomethane (Methyl iodide)	1	0	^E .008	_	.076 (.21)	_	_	_
Methylbenzene (Toluene)	16	81 (13)	^E .3	^E .08	.038 (.05)	1,000	1,000	¹ 2
Methyl tert-butyl ether (MTBE)	1	0	^E .01	_	.112 (.17)	_	20	_
Naphthalene	1	0	^E .03	_	.25 (.25)	_	20	¹ 1.1
Tetrachloroethene	9	0	^E .01	^E .01	.038 (.1)	5	_	¹ 111
Trichloroethene	9	0	^E .01	^E .009	.038 (.038)	5	_	¹ 21
Trichloromethane (Chloroform)	5	0	^E .01	^E .007	.052 (.052)	100	-	¹ 1.8
cis-1,2-Dichloroethene	11	0	^E .03	^E .01	.038 (.038)	70	70	_

¹Environment Canada, 1999

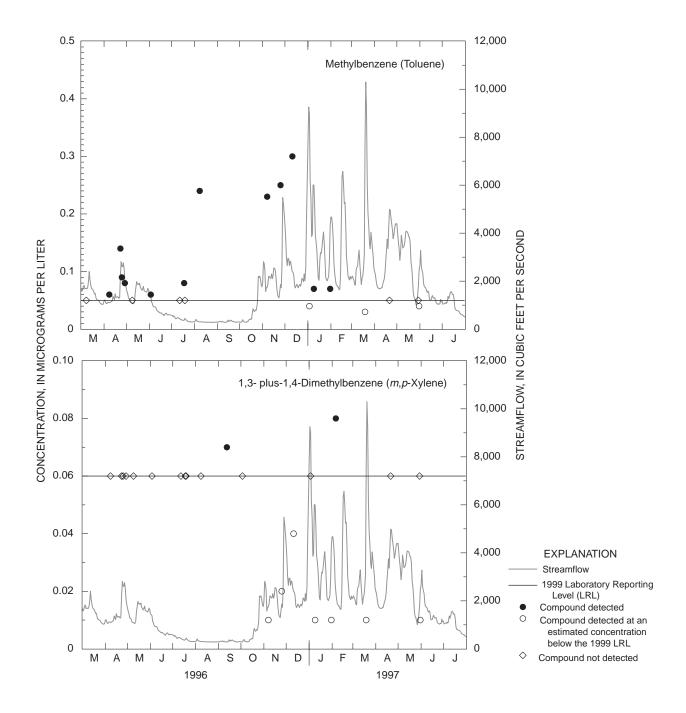


Figure 35. Time series of streamflow and concentrations of selected volatile organic compounds in samples from the Duwamish River (site 6) in the Puget Sound Basin study unit, Washington.

Thornton Creek Basin

The Thornton Creek Basin is a subbasin of the Lake Washington drainage and located entirely within the Puget Sound Lowlands physiographic province. Population density in the basin is high, on the order of 600–1,000 people per square mile. Site 11 (fig. 1 and table 1) was established near where the creek enters Lake Washington. Site 11 is an indicator of a fully developed urban basin, largely residential, but with large shopping malls and commercial development and an interstate freeway bisecting the basin. The creek at site 11 drains an area of 12.1 mi².

Thornton Creek Basin Hydrology

Mean annual streamflow, based on 10 years of record at site 11, was 12.9 ft³/s. Average flow for 7 months of record (March through September) in 1996 was 7.5 ft³/s. Annual flows for water years 1997 and 1998 were 12.7 and 10.2 ft³/s, respectively. Through all of summer 1996, daily streamflows were below normal or near the lower part of the interquartile range (fig. 36). Spring rains caused the creek to rise above the upper quartile on several days in April and May, and rain in early September brought the stream back to normal levels for early fall.

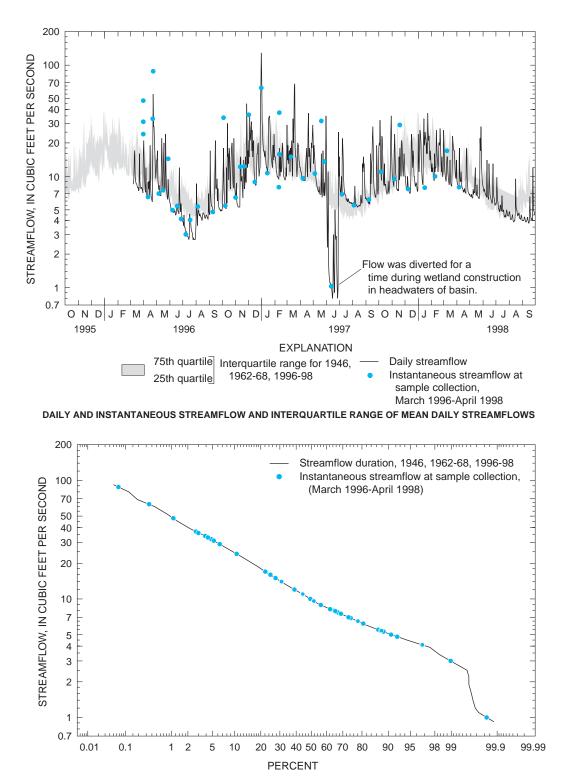
Water year 1997 began with normal streamflows in October and November. Winter 1997-98 streamflows were mostly within the interquartile range but were punctuated by streamflows rising well above the 75th quartile. The snow storm at the end of December and warm temperatures accompanied by heavy rainfall during the New Year's Day 1997 storm produced a flow of 129 ft^3/s , the highest daily flow during the study period. Above-normal precipitation kept flows within the interquartile range or higher in the spring until the end of May. The extreme low flows of June 1997 were the result of water diversions for wetland construction in the upper part of the basin. At the first of July, flows returned to typical levels and remained near the upper quartile to the end of the water year.

During water year 1998, daily flows were mostly within the interquartile range, except at times during rainstorm events or when flows dropped below the 25th quartile, such as in December when precipitation was only about 50 percent of normal (see <u>fig. 3</u>). Most daily flows were below the 25th quartile again in April 1998 at the end of the study period, in response to belownormal precipitation.

Streamflows at the time of sample collection were evenly distributed over the range of flows that occur at this site. Flow magnitudes ranged from high flows that are exceeded less than 0.06 percent of the time to low flows that are exceeded more than 99 percent of the time (fig. 36). The sample collected on December 31, 1996, was during the storm that generated the peak discharge for 1997 and the highest daily flow observed at this site during the study. One sample collected in June 1997 was during the time when the minimum flows were set for the period of record.

Thornton Creek Basin Water Quality

Forty-six water samples from site 11 were collected for the analyses of physical properties, field parameters, and concentrations of inorganic constituents, organic carbon, suspended sediment, and pesticides; 47 samples were collected for VOC analysis (table 22). The water in Thornton Creek was of fair quality. At times, iron and manganese concentrations were large and a number of pesticides and VOCs were present. In one sample, the iron concentration exceeded USEPA drinking-water SMCL of 300 µg/L, and in 11 samples, manganese concentrations exceeded the SMCL of 50 μ g/L (see <u>table 2</u>). On two occasions, water temperature measured at the time of sample collection slightly exceeded the Washington State standard of 18.0°C for a Class A water body, and on one occasion, the pH value at the time of sample collection did not meet the State standards. In samples collected from April 1997-August 1998, concentrations of the fecal-indicator bacteria, E. coli, ranged from 98 to 9,600 col/100 mLs (table 33). Of the 14 samples collected, 9 samples exceeded 298 col/100 mLs, USEPA's (1986b) recommended single-sample concentration for moderate, full-body contact recreation. Of five insecticides detected in samples, concentrations of four did not meet aquaticlife criteria in at least one sample. No other applicable standards and criteria for drinking water, ambient water quality for beneficial uses, and protection of freshwater aquatic life were exceeded by constituent concentrations at this site.



PERCENTAGE OF TIME STREAMFLOWS ARE EQUALED OR EXCEEDED AND INSTANTANEOUS STREAMFLOW

Figure 36. Daily and instantaneous streamflow at the time of sample collection, interquartile range of mean daily streamflows for the period of record, and percentage of time streamflows are equaled or exceeded at Thornton Creek (site 11) in the Puget Sound Basin study unit, Washington.

 Table 22.
 Summary of values of field measurements and concentrations of nutrients, major ions, organic carbon, and suspended sediment in samples from Thornton Creek (site 11) in the Puget Sound Basin study unit, Washington

[Measurement or concentration - Percentile: Percentiles for data sets with 10 percent or more censored data (values less than the MRL) are estimated by log-probability regression (Helsel and Cohn, 1988). Concentrations are dissolved and in milligrams per liter unless otherwise specified. Abbreviations: MRL, minimum reporting level; μ S/cm, microsiemens per centimeter at 25 degrees Celsius; CaCO₃, calcium carbonate; <, less than; μ g/L, micrograms per liter]

	Measurement or concentration										
-				Percentile					Number of samples		
Constituent or property	Mini- mum	10	25	50 (Median)	75	90	Maxi- mum	Number of samples	below MRL (see <u>tables</u> <u>A1-A3</u>)		
Water temperature (degrees Celsius)	3.5	6.2	8.1	11.95	13.7	16.1	18.2	46	0		
Specific electrical conductance (µS/cm)	55	96	176	224	242.5	251	254	46	0		
pH (units)	7.1	7.5	7.8	7.9	8.0	8.1	8.7	46	0		
Dissolved oxygen	8	9.1	9.55	10.45	11.6	12.1	13.9	46	0		
Ammonia nitrogen	< 0.015	< 0.015	0.02	0.05	0.07	0.18	0.47	46	9		
Ammonia-plus-organic nitrogen	<.2	<.2	<.2	.2	.3	.43	1.2	46	15		
Ammonia-plus-organic nitrogen, total	<.2	<.2	<.2	.3	.6	1.18	4.0	46	7		
Nitrite nitrogen	<.01	<.01	<.01	.014	.02	.04	.04	46	14		
Nitrite-plus-nitrate nitrogen	.45	.59	1.00	1.26	1.40	1.60	1.7	46	0		
Phosphorus, total	<.01	.03	.04	.05	.09	.30	1.1	46	1		
Phosphorus	<.01	.01	.02	.03	.04	.06	.28	46	5		
Orthophosphate phosphorus	.01	.02	.02	.03	.04	.06	.10	46	0		
Alkalinity (as CaCO ₃)	16	30	58.5	80.5	87	91	96	46	0		
Bicarbonate (as CaCO ₃)	20	37	71.5	95	106	111	117	46	0		
Calcium	4.9	8.1	15	18	20	21	22	46	0		
Magnesium	1.7	3.5	7.8	11	12	12.8	13	46	0		
Sodium	1.7	3.2	6.1	7.85	8.3	8.7	10	46	0		
Potassium	1.2	1.4	2.1	2.4	2.6	2.7	3.1	46	0		
Chloride	1.3	3.0	5.55	7.05	7.5	8.1	14	46	0		
Sulfate	4.0	7.0	14	17	18	19	20	46	0		
Fluoride	<.1	<.1	<.1	<.1	.1	.1	.11	46	37		
Silica	4.1	8.8	18	25	29	31	34	46	0		
Iron, in μg/L	51	75	97	131	182	200	3,800	46	0		
Manganese, in µg/L	16	23	31	40	50	62	420	46	0		
Dissolved solids, residue at 180 degrees Celsius	39	67	118.5	150.5	162	173	199	46	0		
Organic carbon	2.0	2.4	2.85	3.6	4.55	5.7	9.6	45	0		
Organic carbon, suspended	.2	.2	.3	.45	1.6	6.1	17	46	1		
Sediment, suspended	<1	4	6	8	43.5	135.5	484	44	1		

The concentrations of inorganic compounds were moderately high, as indicated by conductivity, with a median of 224 μ S/cm, and by dissolved solids, with a median of 150 mg/L (table 22). On the basis of median concentrations, calcium and magnesium were the dominant cations and bicarbonate was the dominant anion making up the dissolved solids (fig. 37). Nutrient concentrations were also moderately high, with 75 percent of nitrate concentrations at 1.0 mg/L or higher and phosphorus detected above laboratory MRLs in 90 percent or more samples (table 22). Nearly 25 percent of the concentrations of total phosphorus were greater than 0.1 mg/L, USEPA's (1986a) desired goal to prevent nuisance plant growth in streams. All species of nitrogen analyzed for were present in most samples; however, nitrate, with a median concentration of 1.26 mg/L was the dominant nitrogen species.

In addition to monthly routine samples, 13 of the 46 samples were collected during rainstorms or snowmelt events. Total organic-nitrogen and phosphorus, organic-carbon, and suspended-sediment concentrations varied directly with streamflows, with Kendall's τ correlation coefficients ranging from 0.5 to 0.6 (table 23). The highest nutrient and suspendedsediment concentrations tended to correspond with relatively small runoff events in spring rather than with the large flows (fig. 38). Concentrations of nutrients in filtered water (nitrate and orthophosphate) showed a weak tendency to vary inversely with streamflow $(\tau = -0.4 \text{ and } -0.2, \text{ respectively})$. Dissolved-solids, bicarbonate, and conductivity all varied inversely with streamflows ($\tau = -0.7$ to -0.8). These negative relations generally indicate dilution of the stream's water chemistry by runoff from rain or occasionally snowmelt.

On the basis of the long-term hydrograph for site 11 (see fig. 36), the highest streamflows occur during high-flow periods from October through February, followed by a transition period of gradually diminishing flows from March through June. The lowflow period is from July through September when the stream is at or near baseflow levels. The highest suspended-sediment concentrations were in samples collected during the high-flow and transition periods. On the other hand, medians and interquartile ranges of concentrations indicated nutrient concentrations to be similar across the three periods. The weak but negative correlations of dissolved nutrient concentrations with flow, and generally stable concentrations of the nutrients over the year, suggest a relatively constant source of the dissolved species of nitrogen and phosphorus to the creek, such as from shallow ground water.

Table 23.Correlation between selected water-quality characteristics or
chemical constituents and streamflow for Thornton Creek (site 11) in the
Puget Sound Basin study unit, Washington

Water-quality characteristic or chemical constituent	Kendall's tau correlation coefficient
constituent	Thornton Creek (Site 11)
Specific electrical conductance	-0.73
Dissolved solids	68
Total nitrogen	.23
Dissolved nitrite-plus-nitrate nitrogen	35
Total ammonia-plus-organic nitrogen	.51
Dissolved ammonia-plus-organic nitrogen	.41
Total phosphorus	.46
Dissolved orthophosphate phosphorus	17
Dissolved organic carbon	.48
Suspended organic carbon	.62
Suspended sediment	.60
Bicarbonate	81
Iron	15
Manganese	.07

Thornton Creek Organic Chemistry

A total of 20 pesticides and transformation compounds were detected in samples collected from March 1996 through April 1998 (table 24). Most of the compounds detected were herbicides. The herbicide prometon was detected most frequently, in 45 of 46 samples at concentrations as high as 0.201 μ g/L and with a median of 0.025 μ g/L. Simazine and dichlobenil were the next most frequently detected, in 23 and 21 samples, respectively.

Of the 20 pesticide compounds detected, 5 were insecticides—carbaryl, chlorpyrifos, diazinon, lindane, and malathion. These insecticides are used for pest control on turf, lawns, ornamentals, berries, and structures (see <u>table 27</u>), and all but lindane are readily available to the public through retail sales (Dale Davis, Washington Department of Ecology, written commun., February 1998; Voss and others, 1999).

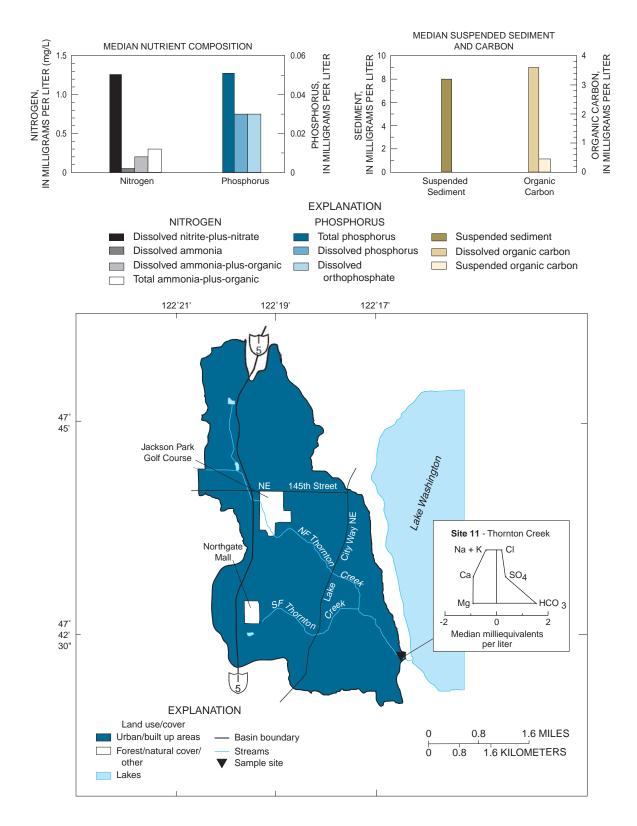


Figure 37. Median concentrations of nutrients, suspended sediment, organic carbon, and major ions in samples from Thornton Creek (site 11) in the Puget Sound Basin study unit, Washington.

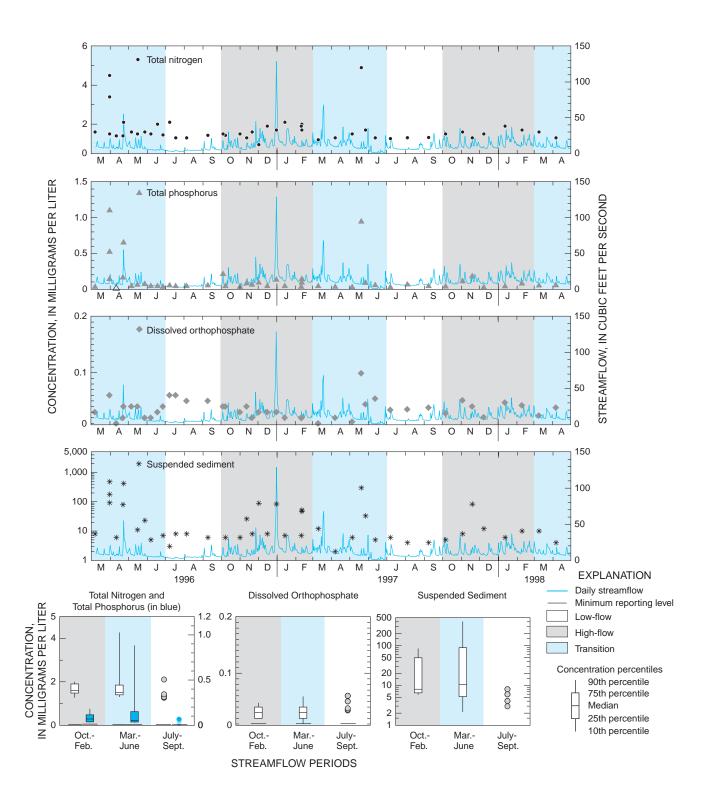


Figure 38. Time series of streamflow and concentrations of total nitrogen, total phosphorus, dissolved orthophosphate phosphorus, and suspended sediment in samples, and concentrations by three streamflow periods, for Thornton Creek (site 11) in the Puget Sound Basin study unit, Washington. (Truncated boxplots of concentration percentiles require a minimum of nine observations, otherwise concentrations are plotted as individual points. Censored data in the time-series graphs are shown as an open symbol. Boxplots are truncated at the minimum reporting level indicated by solid line.)

Table 24. Pesticides in water samples from Thornton Creek (site 11) in the Puget Sound Basin study unit, Washington

[Water-quality criteria – Drinking water: U.S. Environmental Protection Agency (1996). Aquatic organisms – Chronic (USGS): U.S. Geological Survey (1999a). Based on 46 samples collected March 1996 to April 1998; all concentrations are in micrograms per liter (μ g/L); bold type indicates value above aquatic life criterion; method detection limits are from reports by Zaugg and others (1995), Lindley and others (1996), Werner and others (1996), and U.S. Geological Survey National Water Quality Laboratory Technical Memorandums 98.03A and 96.06A; MCL, maximum contaminant level; HAL, Health advisory level; ^E, Estimated–a qualitative value that is less than the statistically determined method detection limit or lowest calibration standard; –, no value or data]

			Median		Water-quality criteria						
Pesticide	Number of	Maximum concentration	concen-	Method detection	Drinkin	g water	Aquatio	: organisms (f	reshwater)		
	detections	value	tration detected	limit	MCL	HAL	Acute	Chronic	Chronic (USGS)		
Atrazine	19	0.006	E0.003	0.001	3	3	¹ 70	¹ 7	1.8		
Carbaryl	4	^E .044	^E .014	.003	_	700	$^{1}0.17$	10.017	0.2		
Chlorpyrifos	3	.074	.015	.004	_	20	² .083	² .041	.041		
DCPA	1	.002	_	.002	_	-	_	_	-		
Deethylatrazine	2	^E .002	-	.002	_	_	_	-	-		
Diazinon	39	.501	.026	.002	_	0.6	³ .16	³ .04	.08		
Dichlobenil	21	^E 1.2	^E .04	1.2	-	-	-	-	_		
Diuron	4	.45	.135	.02	-	10	-	-	_		
EPTC	1	.005	_	.002	-	-	-	_	-		
Lindane	1	.02	_	.004	.2	.2	² .95	4.08	.01		
Malathion	10	.042	.0185	.005	-	200	-	² .1	.1		
MCPA	2	.07	_	.17	-	10	-	_	2.6		
Napropamide	2	.054	_	.003	-	-	-	_	-		
Oryzalin	1	.43	_	.31	_	-	_	_	-		
Prometon	45	.201	.025	.018	-	100	-	-	_		
Pronamide	1	.008	_	.003	-	50	-	_	-		
Simazine	23	.37	.007	.005	4	4	¹ 100	¹ 10	10		
Tebuthiuron	1	.025	-	.01	-	500	-	-	1.6		
Triclopyr	1	.82	-	.25	-	-	¹ 5,600	¹ 560	-		
Trifluralin	2	.007	-	.002	_	5	_	-	.2		

¹ Norris and Dost (1992).

²U.S. Environmental Protection Agency (1998).

³Menconi and Cox (1994).

⁴State of Washington (1992).

The most frequently detected insecticide, diazinon, was detected in 39 samples (85 percent of the samples collected) at concentrations ranging from 0.003 to 0.501 µg/L. Diazinon concentrations in fifteen of these samples exceeded 0.04 µg/L, a limit recommended for the protection of aquatic life by Menconi and Cox (1994) (see <u>table 2</u>). In the 1980's, approximately 83,000 pounds of diazinon were applied within the study unit, about half (39,600 pounds) within King County (Tetra Tech, 1988). Diazinon also is the insecticide purchased at the highest rate by the public through retail outlets in King County (Voss and others, 1999). Two samples had concentrations of carbaryl that

exceeded 0.017 μ g/L, a limit recommended for the protection of aquatic life by Norris and Dost (1992). Lastly, one sample contained chlorpyrifos at a concentration of 0.074 μ g/L, which exceeded the USEPA (1998) aquatic-life criterion of 0.041 μ g/L, and one sample contained lindane at a concentration of 0.02 μ g/L, which exceeded the International Joint Commission Canada and United States (1977) aquatic-life guideline of 0.01 μ g/L. Insecticides purchased by the public for use on lawns and gardens affected the water quality and contributed to the frequency of detections and concentrations above criteria (Voss and others, 1999).

The most frequently observed pesticides at site 11, prometon, simazine, and diazinon, were also the pesticides detected most frequently at urbanindicator sites sampled in NAWQA study units nationwide during 1992-95 (Larson and others, 1997). Most of the concentrations of these frequently detected pesticides at site 11 ranked within the middle-50 percent or within the lowest-25-percent range of concentrations in urban streams studied nationwide in 36 NAWQA study units during 1991–98. Several concentrations, particularly of diazinon, were in the highest-25-percent range of concentrations (Ebbert and others, 2000).

Except for diazinon and prometon, pesticide concentrations were not related to magnitude of streamflows. For prometon and diazinon, concentrations were positively correlated with flow, but the relations were weak (Kendall's τ was 0.4 and 0.5, respectively; p-values less than 0.001). Season and timing of applications appeared to have the greatest influence on pesticide concentrations and detection frequencies. Some of the largest concentrations were in samples collected in spring or early summer from about March through May, particularly if during a rain event. Dichlobenil, rarely detected in winter, was found in most all spring and summer samples (fig. 39). Diazinon concentrations peaked in the spring and again in the fall when applications in urban areas are common. The high concentrations of diazinon at the end of May 1997 and in April 1996 during storms exceeded both the acute $(0.16 \,\mu\text{g/L})$ and chronic $(0.04 \ \mu g/L)$ criteria concentrations recommended by Menconi and Cox (1994) for the protection of aquatic organisms. Both diazinon and prometon, present in so many samples, were detected in relatively high concentrations in baseflow samples as well. The source of relatively high concentrations of diazinon and prometon in some of the baseflow samples was probably precipitation that washed these pesticides into the stream. For example, detections of high concentrations of diazinon and malathion on August 5, 1996, came after 0.74 inch of rain fell on August 2, and it was raining again on the day of collection. In that sample, the maximum concentration of malathion (0.042 μ g/L) and one of the higher values of diazinon (0.13 μ g/L) were observed.

Of the four intensive fixed sites, the Thornton Creek samples contained the most VOCs: 32 compounds (<u>table 25</u>). Ten compounds (acetone, bromoform, trichloromethane, ethylbenzene, dichloromethane, 4-methyl-2-pentanone, methylbenzene, 1,2,4-trimethylbenzene, 1,3-plus-1,4dimethylbenzene, and 1,2-dimethylbenzene) were detected at concentrations above the 1999 LRLs the greatest number of times (see <u>fig. 6</u>). In 80 percent of the samples with VOC detections, concentrations of methylbenzene exceeded the LRL the greatest number of times. Although detections of several VOCs were numerous, no VOC concentration exceeded any established drinking-water or aquatic-life criteria.

A comparison of detections of compounds in concentrations above LRLs with streamflows at the time of sampling indicated that several compounds typically were found during wet winter months (fig. 40). The compounds 1,3-plus-1,4dimethylbenzene, 1,2,4-trimethylbenzene, and 4methyl-2-pentanone were detected mostly between September and May when streamflows were at their highest. Conversely, methylbenzene, acetone, and trichloromethane were detected during both the summer and winter months. Trichloromethane is a byproduct of the chlorination process for drinking-water supplies and its presence in streamwater might indicate mixing of chlorinated water supplies with the stream. Some of the highest trichloromethane concentrations were in samples collected during summer baseflow conditions, indicating that a shallow source, such as shallow ground water or sewer lines, might be contributing trichloromethane to the stream. Additionally, trichloromethane concentrations might be higher during the summer because of the increased outdoor use of chlorinated public water supplies.

Table 25. Volatile organic compounds in water samples from Thornton Creek (site 11) in the Puget Sound Basin study unit, Washington

[Water-quality criteria – Drinking water: U.S. Environmental Protection Agency (1996). Based on 47 samples collected between March 1996 to May 1998; all concentrations are in micrograms per liter (µg/L); MRL, method reporting level (Connor and others, 1998); LRL, laboratory reporting level; MCL, maximum contaminant level; HAL, health advisory level; ^E, Estimated–a qualifier for an analytical result based on the long-term method detection level, laboratory reporting level, and lowest calibration standard (Childress and others, 1999); –, no value or data]

		Percentage				Water-quality criteria			
Volatile organic compound	Number of detections	of detections above 1999 LRL and	Maximum concen- tration value	Median concen- tration detected	MRL (1999 LRL)	Drinkin	g water	Aquatic organisms (freshwater)	
		(number)				MCL	HAL	Chronic	
1,2,3,4-Tetramethylbenzene (Prehnitene)	4	0	^E 0.04	E0.02	0.23 (0.23)	_	Ι	_	
1,2,3,5-Tetramethylbenzene (Isodurene)	2	0	^E .05	_	.24 (.24)	-	-	-	
,2,3-Trimethylbenzene	5	0	^E .03	E.02	.124 (.12)	-	-	-	
1,2,4-Trimethylbenzene	12	33 (4)	.12	^E .035	.056 (.056)	_	-	-	
,2-Dimethylbenzene (o-Xylene)	6	50 (3)	.1	^E .06	.064 (.06)	10,000	10,000	-	
1,3-plus-1,4-Dimethylbenzene (<i>m</i> , <i>p</i> -Xylene)	17	29 (5)	.2	^E .04	.064 (.06)	10,000	10,000	-	
,3,5-Trimethylbenzene	3	0	^E .02	^E .01	.044 (.044)	-	-	-	
,4-Dichlorobenzene	5	0	^E .01	^E .007	.05 (.05)	75	75	¹ 26	
1-Methylethyl)benzene (Isopropylbenzene)	1	0	^E .006	-	.032 (.032)	-	_	-	
P-Butanone (Methyl ethyl ketone)	8	0	1.17	^E .8	1.65 (1.6)	-	-	-	
-Ethyltoluene (o-Ethyl toluene)	5	0	^E .03	^E .01	.1 (.1)	_	_	_	
-Isopropyl-4-methylbenzene (p-Isopropyltoluene)	20	0	^E .044	^E .01	.11 (.11)	-	_	-	
-Methyl-2-pentanone (Methyl isobutyl ketone)	13	54 (7)	^E 1.0	^E .4	.374 (.374)	-	_	-	
Acetone	20	35 (7)	12.5	2.7	4.904 (5)	-	-	-	
Benzene	16	0	^E .1	^E .035	.032 (.1)	5	-	¹ 370	
Bromoform	2	50 (1)	.17	_	.104 (.1)	100	-	-	
Carbon disulfide	14	0	.105	^E .015	.08 (.37)	-	-	-	
Chlorobenzene	1	0	^E .002	-	.028 (.028)	100	100	¹ 1.3	
Chloroethane	2	0	^E .09	-	.12 (.12)	-	-	-	
Chloromethane (Methyl chloride)	15	0	.135	^E .04	.254 (.25)	-	3	-	
Dichloromethane (Methylene chloride)	5	60 (3)	1.36	.45	.382 (.38)	5	-	¹ 98.1	
Diethyl ether	2	0	^E .06	_	.17 (.17)	_	-	-	
Ethenylbenzene (Styrene)	7	0	^E .01	^E .009	.042 (.042)	100	100	-	
Ethylbenzene	8	38 (3)	^E .05	^E .015	.03 (.03)	700	700		
odomethane (Methyl iodide)	1	0	^E .009	-	.076 (.21)	_	-	-	
Aethylbenzene (Toluene)	40	80 (32)	.526	^E .1	.038 (.05)	1,000	1,000	¹ 2	
Japhthalene	10	0	.16	^E .075	.25 (.25)	_	20	¹ 1.1	
Tetrachloroethene	22	0	^E .03	^E .01	.038 (.1)	5	-	¹ 111	
Tetrahydrofuran	1	0	^E .3	-	1.148 (9.0)	-	-	-	
Trichloromethane (Chloroform)	43	28 (12)	.16	^E .04	.052 (.052)	100	-	¹ 1.8	
-Butylbenzene	3	0	^E .01	^E .01	.186 (.19)	_	-	-	
-Propylbenzene	4	0	^E .02	^E .009	.042 (.042)	_	_	_	

¹ Environment Canada (1999).

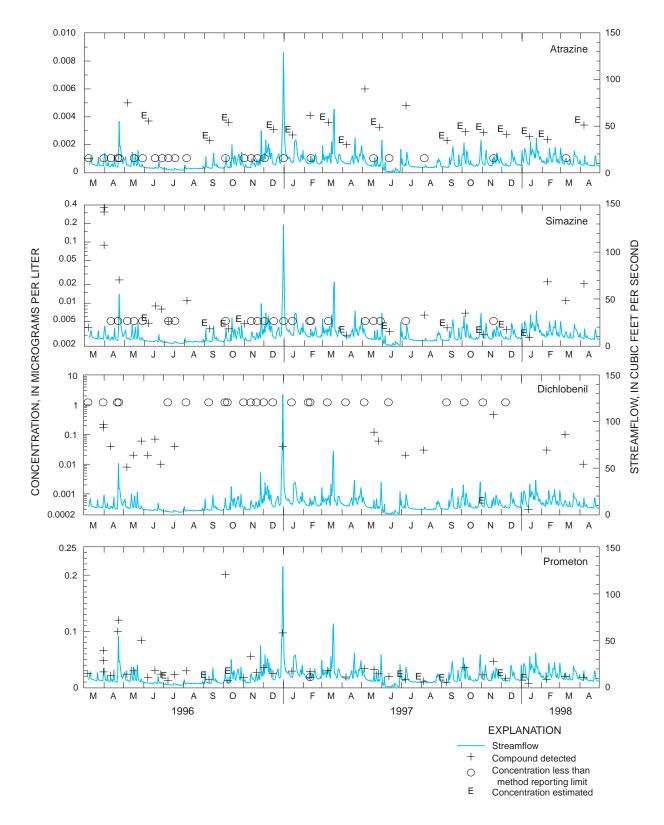
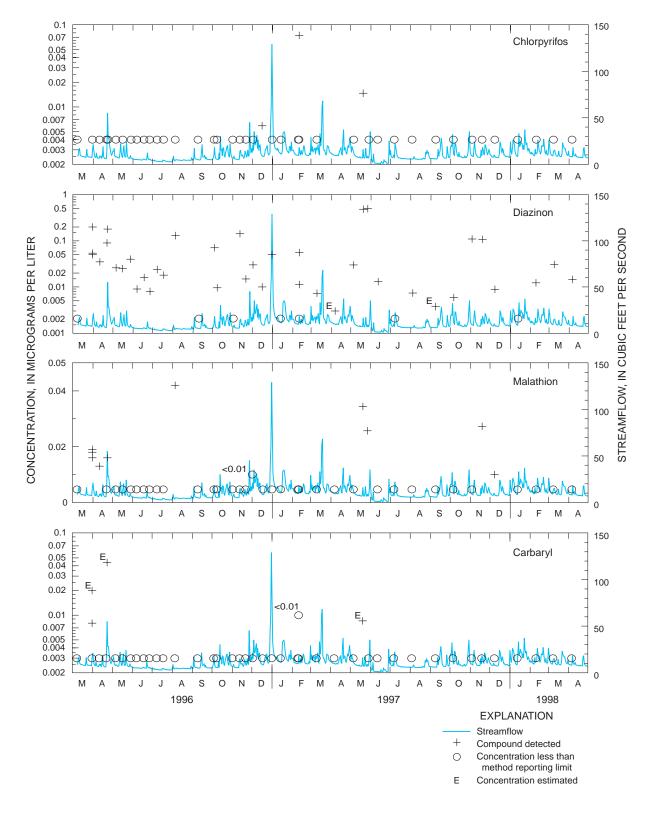


Figure 39. Time series of streamflow and concentrations of selected pesticides detected in samples from Thornton Creek (site 11) in the Puget Sound Basin study unit, Washington.





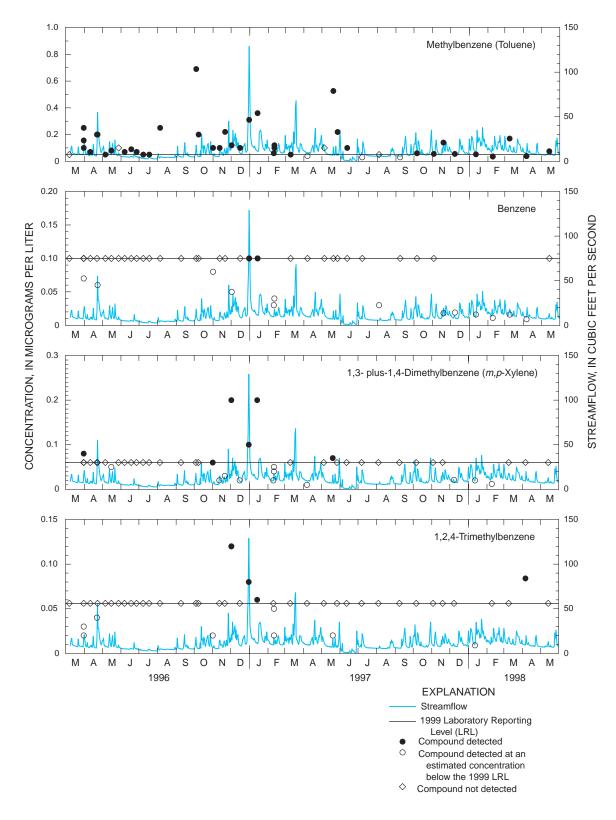


Figure 40. Time series of streamflow and concentrations of selected volatile organic compounds in samples from Thornton Creek (site 11) in the Puget Sound Basin study unit, Washington.

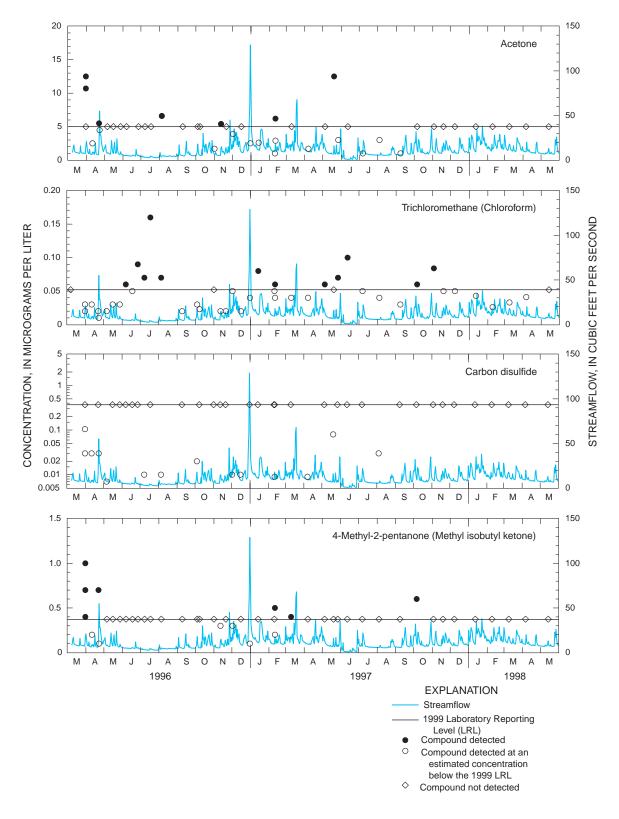


Figure 40. —*Continued*.

LAND USE AND WATER QUALITY

Water-quality conditions at the fixed sites reflect natural characteristics of the watersheds and those resulting from human activities. In the Nooksack and Skokomish Rivers, natural features such as steep gradients, high-energy stream channels, and unstable alluvial streambeds of the mountainous upper watersheds are important factors affecting suspendedsediment concentrations, which can be large during high streamflow events. In summer, water in the Nooksack becomes turbid with a finely ground rock material called glacial flour. It is possible that extensive logging and road building in the Nooksack and Skokomish watersheds are also contributing to the suspended-sediment loads, but the extent of this contribution is unknown. In the forested study basins, dissolved solids and nutrient concentrations were low. At the reference site on the NF Skokomish and the forestry-practices indicator site on the upper Green, natural conditions were reflected in water that was of high quality with low concentrations of dissolved solids, nutrients, and sediment, and standards and criteria that were nearly always met. The other forestry-practices sites (with more than 80 percent forest in their basins), the upper Nooksack and Skokomish, had water of similarly good quality, with some differences that were likely due to natural conditions. For example, some of the large phosphorus concentrations were in samples from the upper Nooksack, indicating that geologic material might be a natural source of phosphorus in this watershed. In general, nutrient concentrations were lowest among the forested sites. In a ranking of the 11 study sites by average nitrogen and orthophosphate concentrations, the reference and the forestry-practices sites ranked near the bottom of the list (table 26).

Unlike the reference and forestry sites with high quality of water, natural conditions might be adversely affecting the quality of water in the urban indicator stream Springbrook, where the sampling reach appears to be in a ground-water discharge zone. The high concentrations of iron and manganese, low dissolvedoxygen concentrations, and perhaps some of the generally high concentrations of phosphorus observed during the study might be attributed to the quality of ground water discharging to this reach. These conditions resulted in iron and manganese concentrations exceeding USEPA SMCLs in most of the samples, and in low concentrations of dissolved oxygen.

Human activities have pronounced effects on water quality at sites in both agricultural and urban basins. Small streams and large rivers in urban and agricultural settings had, on average, higher nitrogen concentration, and small streams had higher orthophosphate concentrations, than the reference stream, NF Skokomish (table 26). Total nitrogen concentrations were highest in the small, agricultural streams (Fishtrap and Newaukum), with averages of about 3 mg/L. Total nitrogen concentrations in the small, urban streams were about half the average concentrations of the agricultural streams (table 26). Among the large rivers integrating a mix of land uses, the lower Nooksack in an agricultural setting, and the Duwamish in an urban setting, had the highest concentrations of total nitrogen. Average total nitrogen in these two rivers exceeded that of the large rivers in forested settings, such as the Skokomish, which had an average total nitrogen concentration of only 0.13 mg/L. On the basis of average orthophosphate concentrations, small urban streams ranked near the top of the list, but the average (0.04 mg/L) was considerably lower than the 0.14 mg/L average concentration for the small agricultural stream, Newaukum Creek.

Table 26. Ranking of 11 large rivers and small streams by average total nitrogen concentrations (the sum of nitrite, nitrate, ammonia, and organic nitrogen) and by average dissolved orthophosphate phosphorus concentrations for the Puget Sound Basin study unit, Washington

[Average total phosphorus concentration: Bold concentrations exceed U.S. Environmental Protection Agency's (1986a) goal to prevent nuisance plant growth in streams. Basin size: Basin size in square miles is shown in table 1. mg/L, milligrams per liter]

		Total nitroge	n		
Large river or small stream (site No.)	Average total nitrogen concentration, in mg/L	Average total phosphorus concentration, in mg/L	Average dissolved orthophosphate phosphorus concentration, in mg/L	Basin size	Land use
Fishtrap (site 4)	3.54	0.086	0.018	small	agriculture
Newaukum (site 9)	2.82	.21	.142	small	agriculture
Thornton (site 11)	1.73	.129	.035	small	urban
Big Soos (site 8)	1.2	.052	.022	small	urban
Springbrook (site 7)	1.1	.165	.035	small	urban
Nooksack at Brennan (site 3)	0.66	.294	.009	large	mixed; agriculture setting
Duwamish (site 6)	.65	.088	.024	large	mixed; urban setting
Nooksack at North Cedarville (site 5)	.39	.148	.005	large	mixed; forestry setting
Skokomish (site 1)	.13	.075	.01	large	mixed; forestry setting
North Fork Skokomish (site 2)	.07	.012	.007	small	reference/undeveloped
Green (site 10)	.07	.012	.012	small	forestry

Dissolved orthophosphate phosphorus												
Large river or small stream (site No.)	Average total nitrogen concentration, in mg/L	Average total phosphorus concentration, in mg/L	Average dissolved orthophosphate phosphorus concentration, in mg/L	Basin size	Land use							
Newaukum (site 9)	2.82	0.21	0.142	small	agriculture							
Thornton (site 11)	1.73	.129	.035	small	urban							
Springbrook (site 7)	1.1	.165	.035	small	urban							
Duwamish (site 6)	0.65	.088	.024	large	mixed; urban setting							
Big Soos (site 8)	1.2	.052	.022	small	urban							
Fishtrap (site 4)	3.54	.086	.018	small	agriculture							
Green (site 10)	.07	.012	.012	small	forestry							
Skokomish (site 1)	.13	.075	.01	large	mixed; forestry setting							
Nooksack at Brennan (site 3)	.66	.294	.009	large	mixed; agriculture setting							
North Fork Skokomish (site 2)	.07	.012	.007	small	reference/undeveloped							
Nooksack at North Cedarville (site 5)	.39	.148	.005	large	mixed; forestry setting							

Pesticides from human activities affected water quality at all four intensively studied sites in both urban and agricultural settings. More types of pesticides were found at the agricultural sites than at the urban sites (fig. 41). Of the four sites, the most pesticides were detected in Fishtrap and more types of pesticides were detected in the lower Nooksack than in the Duwamish. The diversity of pesticides found at the agricultural sites probably reflected the detection of pesticides for urban and domestic use and those used in maintaining rights-of-way in addition to pesticides applied for agricultural purposes. Prometon and tebuthiuron, considered as mostly urban-use herbicides, were quite prevalent in samples from Fishtrap Creek. Both compounds are widely used along roads, railroads, fencelines, and industrial areas for general brush control and on lawns, and both are available to the general public in retail stores (Dale Davis, Washington State Department of Ecology, written commun., February 1998; Voss and others, 1999). The more urbanized areas in the upper part of the basin, the nearby city of Lynden, and the relatively high density of roads, ditches, and levees could all be potential sources of these herbicides to the creek. Some insecticides in samples from Fishtrap, such as carbaryl, might come from urban or agricultural uses, or both. Carbaryl, diazinon, and malathion are available in retail stores and used in urban settings and, along with the insecticides carbofuran, ethoprophos, oxamyl, and propargite, are listed for agricultural applications to beans, strawberries, raspberries, potatoes, and alfalfa (Gianessi and Puffer, 1991 and 1992) (table 27).

Although more types of pesticides were detected in samples from agricultural sites than from urban sites, pesticides were applied in larger quantities in the urban areas. Approximately 783,000 pounds of herbicides (92,500 pounds for agricultural purposes) and 367,000 pounds of insecticides (40,000 pounds for agriculture) were applied annually to the PSB study unit (Tetra Tech, 1988; U.S. Geological Survey, 1999c) (<u>table 27</u>). About 18 percent of the total herbicide applications were within King County, where Thornton Creek and the Duwamish River are located, and 9 percent were within Whatcom County, where Fishtrap Creek and the Nooksack River are located. Detections of insecticides, however, were more frequent and were generally higher in concentration in urban streams than in agricultural streams, probably because of the quantity of insecticide used in urban areas. Thirty-one percent of the total insecticide applications (agricultural and non-agricultural) were within King County and only about 3 percent of the agricultural and non-agricultural applications of insecticides were within Whatcom County. High concentrations of insecticides (which often did not meet aquatic-life criteria) in the urban streams also probably reflected these high percentages of pesticide applications and the availability of insecticides in urban areas.

More VOCs were detected and at a higher detection frequency at the two sites located in urban areas than at the two sites in agricultural areas (fig. 42). For example, 31 compounds were detected in samples from Thornton (100-percent urbanized basin) and 27 compounds were detected in samples from the Duwamish. Conversely, the least number of VOCs (16) were detected at the lower Nooksack, with only 2 percent urban land upstream. Many of the VOCs found at all four sites are fuel related, such as the benzene, methylbenzene, 1,3-plus-1,4-dimethylbenzene, and 1.2-dimethylbenzene compounds. The fuel-related compounds originating from vehicle emissions and perhaps some spills or leaks could enter the streams by direct runoff from streets and highways and from precipitation containing small amounts of dissolved VOCs. MTBE, an automotive fuel additive used in Canada, was found at concentrations below the 1999 LRL in a few samples from Fishtrap, which has about two-thirds of its drainage area in Canada. MTBE is generally not used in Washington and was detected in only one other sample taken at the Duwamish River.

Another group of compounds detected at all sites were trihalomethanes (THM). Trichloromethane was found at all four sites and bromoform was found at all but Fishtrap Creek. THMs can be formed as byproducts from the chlorination of drinking water and trichloromethane is also used as an industrial solvent (Minear and Amy, 1995). The most THM detections and the highest concentrations were in urbanized Thornton, where their presence is likely due to chlorinated public water supplies and possibly to industrial releases into the atmosphere from the greater metropolitan area.

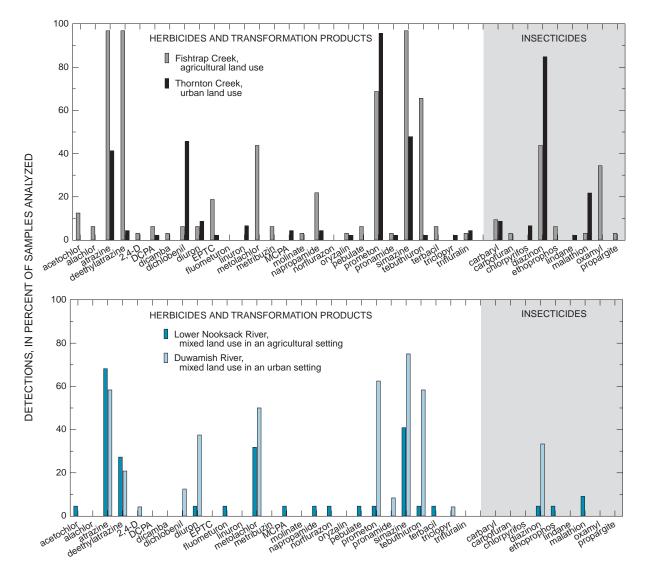


Figure 41. Percentage of detections of pesticides and transformation products in samples from the four intensive fixed sites—lower Nooksack River (site 3), Fishtrap Creek (site 4), Duwamish River (site 6), and Thornton Creek (site 11) in the Puget Sound Basin study unit, Washington.

Table 27. Pesticides detected in water samples from the study sites, the primary use of these pesticides, and estimated pounds of active ingredient applied each year in the Puget Sound Basin study unit, Washington

[Pesticide: 2,4-D, (2,4-dichlorophenoxy) acetic acid; DCPA, dimethyltetrachloroterephthalate; EPTC, S-ethyl dipropylthiocarbamate; MCPA, (4-chloro-2methylphenoxy) acetic acid; HCH, hexachlorocyclohexane. Primary use: Uses compiled from Tetra Tech (1988); Gianessi and Puffer (1991 and 1992); Staubitz and others (1997); Voss and others (1999); Jack Barbash (U.S. Geological Survey, written commun., December 1998); Dale Davis (Washington State Department of Ecology, written commun., February 1998). Estimated applied active ingredient in study unit for agricultural purposes: U.S. Geological Survey (1999c); http://water.wr.usgs.gov/pnsp/anstrat/index.html#hdr1 accessed on February 24, 2000. Estimated applied active ingredient in study unit, and in King and Whatcom Counties: Tetra Tech (1988). –, no value]

		Estimated applie	ed active ingredi per ye		ands of pounds
Pesticide	Primary use	In study unit for agricultural purposes	In study unit	In King County	In Whatcom County
HERBICIDES		92.5	783	141	71.5
Acetochlor	Corn	_	_	_	_
Alachlor	Corn	5.4	9.4	0.8	2.6
Atrazine	Corn, forestry, rights-of-way, Christmas trees ¹	6.0	44.4	18.3	3.6
2,4-D	Agriculture, forestry, urban, wheat, barley, oats, corn, hay, rights-of-way, turf, lawns; available in retail stores	17.4	311	25.2	11.6
Dicamba	Forestry, urban, wheat, corn, seed crops, oats, rights-of-way, fencelines, turf, lawns; available in retail stores	0.9	55.4	19.2	3.6
DCPA	Lawns, turf, ornamentals, seed crops	.2	0.02	.02	-
Dichlobenil	Urban, industrial sites, rights-of-way, golf-courses, under asphalt, raspberries; available in retail stores	.2	7.1	3.5	.3
Diuron	Railways, rights-of-way, ornamentals, ornamental bulbs, seed crops, wheat, oats, raspberries	1.2	37.1	5.4	.3
EPTC	Potatoes, beans, corn, alfalfa, urban residential; available in retail stores	28.4	-	-	-
Fluometuron	Corn (Unknown in the study unit)	_	-	-	-
Linuron	Corn, potatoes, carrots, roadsides, fencelines	.4	_	_	_
Metolachlor	Corn, potatoes, green beans, green peas, turf, fencelines, golf courses (New Jersey)	5.8	5.3	.3	1.8
Metribuzin	Potatoes, alfalfa, grass seed, wheat, green peas, turf grasses	4.5	.3	-	.09
MCPA	Wheat, barley, grass seed, green peas, turf, lawns, urban residential; available in retail stores.	2.3	-	-	-
Molinate	Unknown in study unit; golf courses (Japan); rice elsewhere	-	-	_	-
Napropamide	Strawberries, raspberries, ornamental bulbs, turf, lawns	3.8	.5	.2	.05
Norflurozon	Blueberries and raspberries ¹ , nut trees	1.4	-	_	-
Oryzalin	Urban, ornamental bulbs, lawns, golf courses, blueberries and raspberries ¹ ; available in retail stores	2.4	5.4	3.3	.2
Pebulate	Unknown in the study unit	_	-	-	-
Prometon	Road, railway, fenceline rights-of-way, lawns; industrial sites; urban residential; available in retail stores	_	109	28.3	32.6
Pronamide	Alfalfa, seed crops, raspberries, turf, woody ornamentals, golf courses, forestry	1.8	5.8	.4	.2
Simazine	Raspberries, strawberries, seed crops, turf, golf courses, lawns, aquatic control, brush control	2.7	97.3	19.7	2.6
Tebuthiuron	Pasture, brush control, under asphalt ¹ ; rights-of-way, industrial sites, lawns	-	33.0	8.3	10.3

 Table 27.
 Pesticides detected in water samples from the study sites, the primary use of these pesticides, and estimated pounds of active ingredient applied each year in the Puget Sound Basin study unit, Washington—*Continued*

		Estimated applie	ed active ingredi per yea		ands of pounds
Pesticide	Primary use	In study unit for agricultural purposes	In study unit	In King County	In Whatcom County
HERBICIDES – Conti	nued				
Terbacil	Alfalfa, grass seed, strawberries, raspberries	.5	1.9	-	-
Triclopyr	Forestry brush control, rights-of-way, urban residential, lawns; available in retail stores	_	54.6	7.8	.7
Trifluralin	Potatoes, carrots, green beans, green peas, lawns, golf courses, urban residential; available in retail stores.	7.2	5.5	.4	1.0
INSECTICIDES		40	367	112	11.6
Carbaryl	Beans, strawberries, raspberries, lawns, turf, ornamentals, urban residential; available in retail stores	3.2	37.3	14.2	3.1
Carbofuran	Alfalfa, potatoes, strawberries	3.1	1.7	.4	.1
Chlorpyrifos	Corn, alfalfa, strawberries, structural pest control, lawns, golf courses; urban residential; available in retail stores	6.1	39.4	18.5	1.6
Diazinon	Berries, potatoes, row crops, household insects, lawns, urban residential; available in retail stores	5.8	83.1	39.6	3.5
Ethoprophos	Potatoes, turf, golf courses	8.0	-	-	-
Lindane (gamma-HCH)	Urban insecticide for Puget Sound (Tetra Tech, 1988)	_	2.6	1.3	.1
Malathion	Alfalfa, fruits, ornamentals, strawberries, blueberries, raspberries; available in retail stores	6.2	203	38.0	3.2
Oxamyl	Raspberries in Canada, potatoes in Washington State (Inkpen and others, 2000) Potatoes in Gianessi and Puffer (1990)	2.3	-	-	_
Propargite	Christmas trees, conifers, ornamentals, potatoes, alfalfa, strawberries	5.3	-	-	_

¹ Reported for use in the Willamette Basin study by Anderson and others (1996).

Many solvents were found in surface-water samples, particularly those samples taken from the Duwamish and Thornton. Carbon disulfide, chloromethane, and 4-methyl-2-pentanone were the most commonly detected solvents and were found at all four sites. However, many solvents were only found at the more urbanized sites. For example, the chlorinated solvents trichloroethene (TCE) and tetrachloroethene (PCE) were detected only in Duwamish and Thornton samples. The only VOC that was distinctly for agricultural use was 1,2-dichloropropane, detected only in Fishtrap Creek (fig. 42). Historically, 1,2-dichloropropane was used as a soil fumigant and its use has been banned; however, at the time of this study, it was still contained in minute amounts in formulations of 1,3dichloropropene (Zebarth and others, 1998). Although 1,3-dichloropropene has not been sold in Canada since 1993 (Zebarth and others, 1998), it was still applied in the Washington State part of Fishtrap Creek Basin (Cindy Moore, Washington State Department of Agriculture, written commun., 1998) and might be a source of the 1,2-dichloropropane.

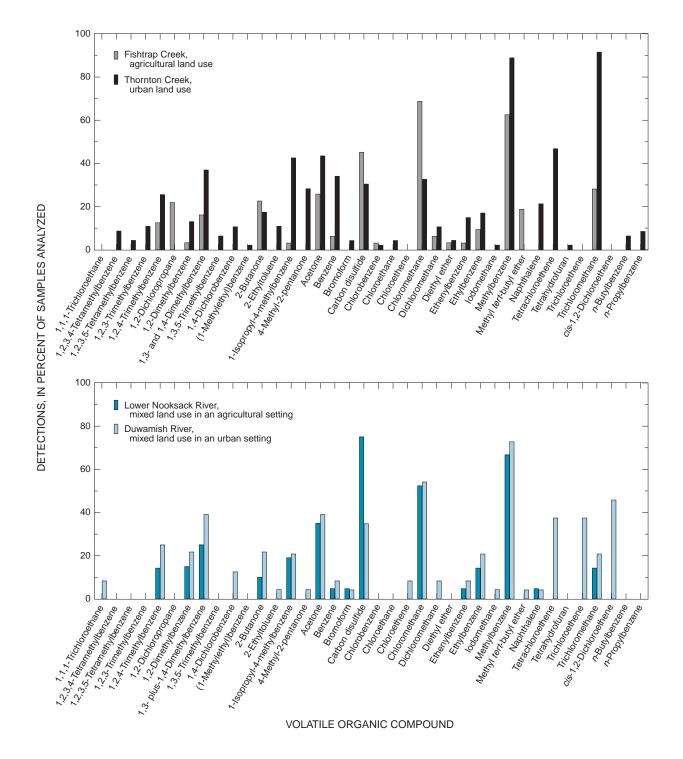


Figure 42. Percentage of all detections of volatile organic compounds in samples from the four intensive fixed sites—lower Nooksack River (site 3), Fishtrap Creek (site 4), Duwamish River (site 6), and Thornton Creek (site 11) in the Puget Sound Basin study unit, Washington.

LOADS AND YIELDS

An estimate of loads is useful for assessing the quantity of constituents transported by rivers to receiving bodies of water, such as Puget Sound and Lake Washington, and for comparing yields of these constituents for river basins with different characteristics and land-use activities. In this study, the maximum likelihood estimation method (MLE) was selected for estimating loads of total nitrogen (using the sum of nitrite, nitrate, ammonia, and organicnitrogen concentrations), phosphorus (using concentrations determined on unfiltered water), and orthophosphate (using concentrations determined on filtered water) at all 11 sites. This selection was based on several factors described in Appendix C, which details the load estimates and provides graphs of predicted and measured daily loads, graphs of nutrient and suspended-sediment concentrations plotted as a function of streamflow, and tables of the regression equations, annual average loads and their standard deviations.

In general, the standard deviations for totalnitrogen load estimates were smaller than those for the phosphorus-load estimates, possibly because there were fewer censored values in the nitrogen data sets than in the phosphorus data sets (Appendix tables C1-C3). Nitrogen, in at least the nitrite-plus-nitrate form, was nearly always detected at concentrations above the MRL, whereas phosphorus and orthophosphate were typically detected at low concentrations and a high percentage were censored at the MRL. With 36 to 42 percent of their data sets censored, the standard deviations for total nitrogen loads at the NF Skokomish and upper Green Rivers were about 9 and 2 tons per year, or 18 and 40 percent of their annual total nitrogen loads, respectively (Appendix table C1). Predicted daily and annual loads of total nitrogen from the regression equations agreed reasonably well with measured loads at most sites.

With 41 to 73 percent of their data sets censored, the estimates of annual phosphorus loads in the Skokomish and NF Skokomish had standard deviations of 40 and 73 percent, respectively (Appendix <u>table C2</u>). The annual orthophosphate load in the NF Skokomish had a standard deviation of 9 percent (Appendix <u>table C3</u>). At most sites the predicted annual loads of phosphorus and orthophosphate appeared reasonable when compared to measured loads, even though daily loads could be quite different. During parts of the wet season of water year 1997, the equations tended to overpredict daily loads of phosphorus or orthophosphate at some sites.

Suspended-sediment loads were estimated by the MLE method at 7 of the 11 sites. At the other four sites, the linear attribution estimation (LAE) method was selected because the rate of censoring was low (less than 20 percent of the observations) and test statistics indicated a non-normal distribution of the residuals from the concentration-flow regression. Sites with the largest standard deviations for annual suspendedsediment loads included the upper Green, with a standard deviation of more than 100 percent, Big Soos with 56 percent, the Skokomish with 48 percent, and the NF Skokomish with 46 percent (Appendix table C4). Although predicted daily loads of suspended sediment could be quite different from measured, the predicted annual loads appeared reasonable when compared with measured annual loads. The exceptions were the above four sites, for which large standard deviations and percent differences between measured and predicted loads indicate that results for these sites should be viewed with caution.

Loads are directly related to streamflow, and therefore are largest during periods of high streamflow and are generally largest from those watersheds with big drainage areas. Nutrient loads transported during the runoff and high streamflow periods of the rainy fall and winter seasons greatly exceeded summertime loads. For total nitrogen and phosphorus, average daily loads in winter were typically 2 to 3 orders of magnitude greater than average daily loads in summer. Nutrient loads estimated for the 11 sites ranged from 6.0 to 3,200 ton/yr of total nitrogen and from about 2 to 890 ton/yr of phosphorus, with the smaller values corresponding to the upper Green River (drainage area of 16.5 mi²) and the larger values corresponding to the lower Nooksack (drainage area of 790 mi²) (fig. 43).

Yields in this study are constituent loads per unit of drainage area and allow comparisons to be made among sites with different basin characteristics. Annual average nutrient yields ranged from 0.4 to 8.8 ton/mi² (tons per square mile) of total nitrogen in the upper Green and Fishtrap, respectively, and from about 0.1 ton/mi² of phosphorus in Thornton and the upper Green, to 1.2 ton/mi² of phosphorus in the upper Nooksack. Of the three major study basins, nutrient yields were largest from the Nooksack River Basin and smallest from the Skokomish River Basin (fig. 44).

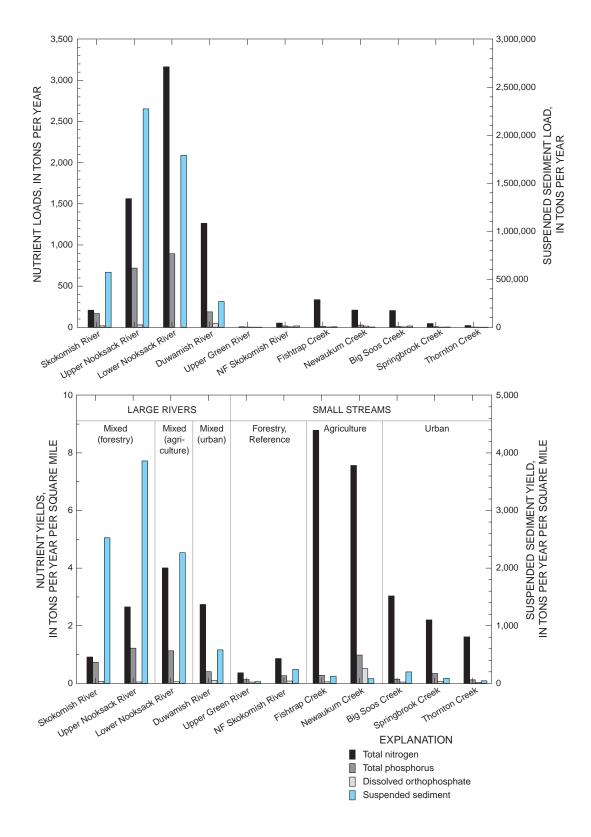


Figure 43. Nutrient loads transported in surface water at study sites, and nutrient yields from the basins by major land-use categories, in the Puget Sound Basin study unit, Washington.

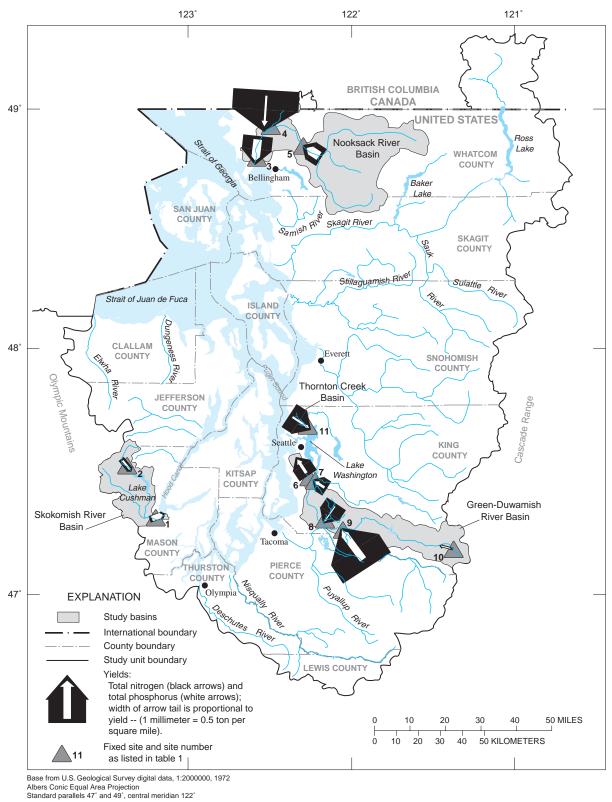


Figure 44. Nutrient yields, 1996–98, from study basins in the Puget Sound Basin study unit, Washington.

This is consistent with previous work in the PSB, which showed nutrient yields to be highest from basins dominated by agricultural land-use practices and related to source-loading rates from animal manures, fertilizers, and precipitation (Embrey and Inkpen, 1998). The Nooksack River Basin was estimated to receive 9.1 tons of nitrogen and 1.3 tons of phosphorus per square mile of drainage basin, which were among the highest source-loading rates estimated for the major PSB watersheds (Embrey and Inkpen, 1998). The Skokomish River Basin had one of the lowest rates, receiving 0.4 ton of nitrogen and 0.2 ton of phosphorus per square mile of drainage basin. From Fishtrap and Newaukum Creeks, the two streams indicative of water quality from agricultural basins, total nitrogen yields were the highest of all 11 streams (fig. 43).

The annual average nutrient yields from the urban and suburban basins, ranging from 1.6 ton/mi² of total nitrogen from Thornton Creek to 3.0 ton/mi² of total nitrogen from Big Soos Creek, were also well above those from the reference and forestry basins (figs. 43 and 44). Nutrient source loading to the Green-Duwamish River Basin, which includes Big Soos, was estimated at 4.5 ton/mi² of nitrogen and 0.69 ton/mi² of phosphorus (Embrey and Inkpen, 1998). Precipitation was an important part of this source loading, contributing 1.1 ton/mi² of nitrogen and 0.12 ton/mi² of phosphorus. However, because the data were unavailable, a potentially important nutrient contribution was not included in total source-loading estimates for urban watersheds-the loading from residential and commercial fertilizer applications, as well as unknown amounts from miscellaneous waste such as leaking sewers, pets and wildlife, or failing septic systems.

In contrast to nitrogen, phosphorus yields were more variable among the land-use categories. For example, the yield of phosphorus from the Skokomish, with very little agricultural land use in the basin, was at least twice that of Fishtrap Creek, with largely agricultural land use. And even though both Fishtrap and Newaukum are in agricultural basins, Fishtrap yielded more total nitrogen (about 1 ton/mi² more) but less phosphorus (about one-third less). Natural sources of phosphorus, in association with suspended sediment, might account for some of the variation observed in total phosphorus yields. Phosphorus yields tended to correspond to suspended-sediment yields at most of the sites (fig. 45).

Compared with loads estimated by Embrey and Inkpen (1998) using historical data collected mostly by State and county agencies, inorganic-nitrogen and phosphorus loads were generally higher during this 1996–98 study. A combination of factors probably contributed to these differences, including sampling methods (discharge-weighted sample collection used in this study) and the inclusion of several storm and floodevent samples collected during this study, which contributed high nutrient concentrations to the data sets. In particular, above-normal streamflows during 1996 and 1997 would have resulted in higher load calculations for this study.

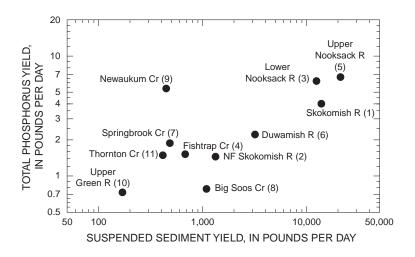


Figure 45. Relation between total phosphorus and suspended-sediment yields, 1996–98, for the 11 river basins in the Puget Sound Basin study unit, Washington

Skokomish River Basin

During the study, the Skokomish transported about 210 ton/yr of total nitrogen, 170 ton/yr of phosphorus, and 16 ton/yr of orthophosphate to Hood Canal. The load of suspended sediment amounted to about 570,000 ton/yr (table 28). Except for orthophosphate, the highest loads of the study period were transported during 1996 and 1997, and the lowest in 1998. About 71 percent of the total nitrogen load, or 150 ton/yr, was composed of inorganic nitrogennitrate, nitrite, and ammonia. The inorganic nitrogen load of this study was essentially the same as the 170 ton/yr estimated for the historical period of 1980-93 (Embrey and Inkpen, 1998). The phosphorus load, however, was more than 2.5 times the 60 ton/yr estimated for the historical period because of abovenormal streamflows during the study and higher phosphorus concentrations. Twenty-five percent of phosphorus concentrations observed during this study were greater than 0.06 mg/L, whereas less than 10 percent of the historical data exceeded 0.06 mg/L.

Nutrient loads transported during fall and winter greatly exceeded summertime loads. In winter, the Skokomish transported an average of about 2,600 lb/day (pounds per day) of total nitrogen, 2,100 lb/day of phosphorus, and 7,000,000 lb/day of suspended sediment. With lower flows in summer, the average loads dropped to about 170 lb/day of total nitrogen, 15 lb/day of phosphorus, and 10,000 lb/day of suspended sediment.

The NF Skokomish transported 49 ton/yr of total nitrogen, 15 ton/yr of phosphorus, and 4.5 ton/yr of orthophosphate to Lake Cushman during the study. The load of suspended sediment amounted to 14,000 ton/yr (table 28). About 90 percent of the total nitrogen load, or 44 ton/yr, was composed of inorganic nitrogen. During winter, in response to increased streamflows, the NF Skokomish transported an average of 420 lb/d of total nitrogen, 150 lb/d of phosphorus, and 140,000 lb/d of sediment. In summer, the average loads were reduced to about 120 lb/d of total nitrogen, 10 lb/d of phosphorus, and 2,700 lb/d of suspended sediment.

Table 28. Loads and basin yields during 1996, 1997, and 1998 and their averages for the study period 1996-98; average loads for the historical period 1980-93; and daily loads, by season, for the study period 1996-98 at site 1 and site 2, Skokomish River Basin, in the Puget Sound Basin study unit, Washington

[-, not calculated; ton/mi², tons per square mile]

			T	otal nitro	gen loa	ds and	yields		Inorganic nit (tons per	•	Total nitrogen load, by season (pounds per day)			
Site name	Yearl	y load	(tons)	Yearly	yield (to	n/mi²)	Annual	Annual	For study period	For				
(site No.) 1	1996	1997	1998	1996	1997	1998	average load for 1996-98 (tons)	average yield for 1996-98 (ton/mi ²)	1996-98 (Percentage of total nitrogen load)	historical period 1980-93	Winter	Spring	Summer	Fall
Skokomish River (1)	260	200	170	1.1	0.88	0.75	210	0.91	150 (71)	170	2,600	660	170	1,200
North Fork Skokomish River (2)	50	52	46	.87	.91	.80	49	.86	44 (90)	-	420	290	120	250

					Phosp	ohorus la	ads and yield	S		Phosphorus loads, by season (pounds per day)				
Site name	Year	y load ((tons)	Yearly	yield (to	on/mi ²)	Annual	Annual	Annual average					
(site No.)	1996	1997	1998	1996	average average load for load for yield for bistorical j 996 1997 1998 1996-98 1996-98	load for the historical period 1980-93 (tons)	Winter	Spring	Summer	Fall				
Skokomish River (1)	220	170	100	0.97	0.75	0.44	170	0.73	60	2,100	760	15	760	
North Fork Skokomish River (2)	16	22	8	.28	.38	.14	15	.26	_	150	100	10	73	

				Orthopho	osphate j	ohosphor	us loads and	l yields		Orthophosphate phosphorus loads, by season (pounds per day)					
Site name	Yearl	y load (tons)	Yearly	y yield (to	on/mi²)	Annual	Annual	Annual						
	1996	1997	1998	1996	1997	1998	average load for 1996-98 (tons)	average yield for 1996-98 (ton/mi ²)	average load for the historical period 1980- 93 (tons)	Winter	Spring	Summer	Fall		
Skokomish River (1)	14	16	17	0.06	0.07	0.07	16	0.07	13	190	62	22	79		
North Fork Skokomish River (2)	2	4	7	.03	.07	.12	4.5	.08	_	37	21	13	28		

Table 28. Loads and basin yields during 1996, 1997, and 1998 and their averages for the study period 1996-98; average loads for the historical period 1980-93; and daily loads, by season, for the study period 1996-98 at site 1 and site 2, Skokomish River Basin, in the Puget Sound Basin study unit, Washington—*Continued*

			Su	spended	-sedime	nt loads a	and yields			Suspended-sediment loads, by season, (pounds per day)				
Site name (site No.)	Yearly load (tons) 1996 1997 1998			Yearly yield (ton/mi ²)		Annual average load for 1996-98	Annual average yield for 1996-98	Annual average load for the historical period	Winter	Spring	Summer	Fall		
							(tons)	(ton/mi ²)	1980-93 (tons)					
Skokomish River (1)	790,000	660,000	260,000	3,500	2,900	1,100	570,000	2,500	_	7,000,000	3,200,000	10,000	2,400,000	
North Fork Skokomish River (2)	17,000	18,000	6,700	300	310	120	14,000	240	-	140,000	68,000	2,700	96,000	

Annual total nitrogen and orthophosphate yields were similar for both sites in the Skokomish River Basin (fig. 44). At both sites, the total nitrogen yields were 0.9 ton/mi² per year; at site 1 and site 2, the orthophosphate yields were 0.07 and 0.08 ton/mi² per year, respectively. The phosphorus yield from the basin at site 1 (0.73 ton/mi² per year), however, was more than double the yield $(0.26 \text{ ton/mi}^2 \text{ per year})$ from the NF Skokomish River Basin at site 2. Source-loadings to the Skokomish River Basin from agricultural activities and precipitation were estimated to be about 0.4 ton/mi^2 total nitrogen and 0.2 ton/mi^2 phosphorus (Embrey and Inkpen, 1998). Because the NF Skokomish is the study's reference basin, the loads at site 2 represent background levels of riverine nutrient transport and nutrient loadings to PSB watersheds from natural sources, such as rock weathering, biological fixation, and precipitation. Yields of similar magnitude as site 2 indicated that much of the total nitrogen and orthophosphate transported from the Skokomish River Basin at site 1 is from natural sources. However, the considerably larger phosphorus and suspendedsediment yields at site 1 than at site 2 indicated that forestry practices, roads, and other human activities in the lower Skokomish River Basin and in the SF Skokomish River Basin added to the phosphorus and suspended-sediment loads observed at site 1.

Nooksack River Basin

During the 1996–98 study, the lower Nooksack River transported 3,200 ton/yr of total nitrogen, 890 ton/yr of phosphorus, and 43 ton/yr of orthophosphate to Bellingham Bay. The load of suspended sediment was about 1,800,000 ton/yr (table 29). The highest loads were transported during 1996 and 1997, and the lowest in 1998. About 62 percent of the total nitrogen load, or 2,000 ton/yr, was composed of inorganic nitrogen-nitrate, nitrite, and ammonia. This inorganic nitrogen load was not much different from the 1,700 T/yr for the historical period of 1980-93 (this value is revised from the value published by Embrey and Inkpen, 1998). However, as a result of above-normal streamflows in 1996 and 1997 and higher concentrations, the phosphorus load was about four times larger than the 260 ton/yr estimated for the historical period. Twenty-five percent of phosphorus concentrations observed during this study were greater than 0.17 mg/L, whereas less than 10 percent of the historical data exceeded 0.17 mg/L. Nutrient loads transported during fall and winter greatly exceeded summertime loads. In winter, the lower Nooksack transported an average of 35,000 lb/d of total nitrogen, 7,600 lb/d of phosphorus, and 13,000,000 lb/d of suspended sediment. In response to lower flows in summer, the average loads dropped to 4,800 lb/d of total nitrogen, 1,600 lb/d of phosphorus, and 4,500,000 lb/d of suspended sediment.

Table 29. Loads and basin yields during 1996, 1997, and 1998 and their averages for the study period 1996-98; average loads for the historical period 1980-93; and daily loads, by season, for the study period 1996-98 at site 3, site 4, and site 5, Nooksack River Basin, in the Puget Sound Basin study unit, Washington

[-, not calculated; ton/mi², tons per square mile]

			To	tal nitro	gen loa	ds and y	vields		Inorganic niti (tons per	0	d Total nitrogen load, by season (pounds per day)				
Site name	Year	rly load	(tons)	Yearly	yield (to	on/mi²)	Annual	Annual	For study period	For					
(site No.)	1996	1997	1998	1996	1997	1998	average load for 1996-98 (tons)	average yield for 1996-98 (ton/mi ²)	1996-98 (Percentage of total nitrogen load)	historical period 1980-93	Winter	Spring	Summer	Fall	
Nooksack River (3)	3,500	3,700	2,300	4.4	4.7	2.9	3,200	4.0	2,000 (62)	¹ 1,700	35,000	12,000	4,800	18,000	
Fishtrap Creek (4)	-	420	250	-	11	6.6	330	8.8	280 (85)	-	3,600	2,100	570	1,100	
Nooksack River (5)	1,700	1,900	1,100	2.9	3.2	1.9	1,600	2.7	830 (52)	750	14,000	5,100	3,000	12,000	

					Phosp	ohorus la	ads and yield	S		Phosphorus loads, by season (pounds per day)				
Site name	Year	y load (tons)	Yearly	yield (to	on/mi²)	Annual	Annual	Annual average					
	1996	1997	1998	1996	1997	1998	average load for 1996-98 (tons)	average yield for 1996-98 (ton/mi ²)	load for the historical period 1980-93 (tons)	Winter	Spring	Summer	Fall	
Nooksack River (3)	1,200	1,100	400	1.5	1.4	0.51	890	1.1	260	7,600	2,400	1,600	8,100	
Fishtrap Creek (4)	_	15	6	-	0.39	.16	11	0.28	-	130	60	10	34	
Nooksack River (5)	740	1,100	340	1.3	1.9	.58	720	1.2	160	5,600	3,400	1,800	5,000	

				Orthopho	osphate	phosphor	us loads and	l yields		Orthophosphate phosphorus loads, by season (pounds per day)					
Site name	Yearl	y load (tons)	Yearly	yield (to	on/mi²)	Annual	Annual	Annual average						
(site No.) 1	1996	1997	1998	1996	1997	1998	average load for 1996-98 (tons)	average yield for 1996-98 (ton/mi ²)	load for the historical period 1980- 93 (tons)	Winter	Spring	Summer	Fall		
Nooksack River (3)	44	53	34	0.06	0.07	0.04	43	0.06	44	320	230	170	230		
Fishtrap Creek (4)	-	3	1	-	.08	.03	2.0	.05	_	24	11	2	7		
Nooksack River (5)	_	-	-	-	-	-	6-40	.0107	21	_	-	_	_		

Table 29. Loads and basin yields during 1996, 1997, and 1998 and their averages for the study period 1996-98; average loads for the historical period 1980-93; and daily loads, by season, for the study period 1996-98 at site 3, site 4, and site 5, Nooksack River Basin, in the Puget Sound Basin study unit, Washington—*Continued*

			Suspe	nded-se	diment l	oads and	yields			Suspended-sediment loads, by season, (pounds per day)				
	Yea	rly load (tor	ıs)	Yearly	yield (to	on/mi ²)			Annual average					
Site name (site No.)	1996	1997	1998	1996	1997	1998	Annual average load for 1996-98 (tons)	Annual average yield for 1996-98 (ton/mi ²)	load for the histori- cal period 1980-93 (tons)	Winter	Spring	Summer	Fall	
Nooksack River (3)	2,400,000	2,300,000	690,000	3,000	2,900	870	1,800,000	2,300	-	13,000,000	6,300,000	4,500,000	15,000,000	
Fishtrap Creek (4)	-	6,900	2,600	-	180	68	4,700	120	-	58,000	27,000	4,300	15,000	
Nooksack River (5)	2,300,000	3,700,000	800,000	3,900	6,300	1,400	2,300,000	3,900	-	12,000,000	14,000,000	8,600,000	15,000,000	

¹This value was published as 1,400 in Embrey and Inkpen (1998); since revised to 1,700.

The tributary Fishtrap Creek transported 330 ton/yr of total nitrogen, 11 ton/yr of phosphorus, and 2.0 ton/yr of orthophosphate to the lower Nooksack. The load of suspended sediment was about 4,700 ton/yr (table 29). Constituent loads transported in 1997 were about twice as large as loads transported in 1998. About 85 percent of the total nitrogen load, or 280 ton/yr, was composed of inorganic nitrogen. In winter, Fishtrap transported an average of 3,600 lb/d of total nitrogen, 130 lb/d of phosphorus, and 58,000 lb/d of sediment. In summer, the average loads dropped to 570 lb/d of total nitrogen, 10 lb/d of phosphorus, and 4,300 lb/d of suspended sediment.

The upper Nooksack River transported 1,600 ton/yr of total nitrogen, 720 ton/yr of phosphorus, and 2,300,000 ton/yr of suspended sediment at the sampling site at North Cedarville (table 29). An estimate using the Beale ratio (Crawford, 1996) indicated that orthophosphate loads ranged from 6 to 40 ton/yr. The river at North Cedarville transported the highest loads of nutrients and suspended sediment for the 3-year study in 1997. Fifty-two percent of the total nitrogen load, or 830 ton/yr, was composed of inorganic nitrogen; thus, at 48 percent, organic nitrogen was an important component of the total nitrogen load. As in the lower Nooksack, the inorganic nitrogen load of this study was only slightly larger than the load of 750 ton/yr and the phosphorus load was about four times larger than the load of 160 ton/yr estimated for the historical period of 1980–93 (Embrey and Inkpen, 1998). Fifty percent of phosphorus concentrations observed during this study were greater than 0.03 mg/L, whereas only 25 percent of the historical data exceeded 0.03 mg/L. In response to higher streamflows and concentrations, the upper Nooksack transported in winter an average of 14,000 lb/d of total nitrogen and 5,600 lb/d of phosphorus, which were much higher than loads transported during summer low flows. Suspended sediment transported during winter averaged 12,000,000 lb/d, but dropped to 8,600,000 lb/d in summer.

In terms of unit area, the annual total nitrogen yield from the Nooksack River Basin at site 3 was 4 ton/mi² (fig. 44). This increase of 1.3 ton/mi² over the total nitrogen yield from the upper Nooksack River Basin at site 5 is indicative of the more intensive agricultural land-use activities in the lower Nooksack River Basin. Fishtrap Creek at site 4 yielded 8.8 ton/mi² of total nitrogen to the lower Nooksack. Nitrogen-source loadings each year to the Nooksack watershed from animal manures, agricultural fertilizers, and precipitation was estimated to be about 9 ton/mi², with more than half the loading from animal manures (Embrey and Inkpen, 1998). The annual phosphorus yield of 1.1 ton/mi^2 and the orthophosphate yield of 0.06 ton/mi^2 from the lower basin at site 3 were essentially the same as the yields from the upper basin at site 5 (fig. 44), indicating that the main sources of phosphorus to the Nooksack River are in the upper basin. Yields of only 0.28 ton/mi^2 of phosphorus and 0.05 ton/mi^2 of orthophosphate from Fishtrap Creek at site 4 indicated that the lowland tributary basins yield relatively small amounts of phosphorus to the lower Nooksack River.

In addition to phosphorus, the upper basin is also the main source of suspended sediment in the lower Nooksack. At site 5, the upper Nooksack yielded 3,900 ton/mi² of suspended sediment, a large portion of which is lost by settling or by dilution within the reach downstream from site 5 to site 3. At site 3, the suspended-sediment yield was 2,300 ton/mi². Although some agriculture exists in the upper Nooksack watershed, land use is mostly a combination of undeveloped terrain, forestry practices, and road building, and the latter two are reported to be important sources of suspended sediment (U.S. Forest Service, 1995) in the river. Other sources of nutrients and suspended sediment to the Nooksack River Basin include natural sources such as rock weathering, biological fixation, and precipitation.

Green-Duwamish River Basin

During the 1996–98 study, the Duwamish River transported an average of 1,300 ton/yr of total nitrogen, 190 ton/yr of phosphorus, and 44 ton/yr of orthophosphate to Puget Sound. About 270,000 ton/yr of suspended sediment were transported to the Sound. The river transported the highest loads during 1996 and 1997 and the lowest in 1998 (table 30). Sixty-six percent of the total nitrogen load, or 860 ton/yr, was composed of inorganic nitrogen-nitrate, nitrite, and ammonia, which was about 60 percent larger than the 520 ton/yr estimated by Embrey and Inkpen (1998) for the historical period 1980-93. The phosphorus load of this study was about twice the estimate for the 1980-93 historical period. Above-normal streamflows and higher concentrations account for the higher nutrient loads estimated for this 1996-98 study. Concentrations of ammonia and of nitrite-plus-nitrate nitrogen observed in this study were generally higher than the historical data, and 25 percent of phosphorus concentrations observed during this study were greater than 0.1 mg/L, whereas less than 10 percent of the historical data exceeded 0.08 mg/L. In response to higher streamflows, loads transported during fall and winter greatly exceeded summertime loads. In winter, the Duwamish transported an average of 15,000 lb/d of total nitrogen, 2,300 lb/d of phosphorus, and 710,000 lb/d of suspended sediment. With low flows and low concentrations in summer, the average loads dropped to about 1,700 lb/d of total nitrogen, 200 lb/d of suspended sediment.

Springbrook transported an average of 44 ton/yr of total nitrogen, 6.9 ton/yr of phosphorus, and 1.3 ton/yr of orthophosphate to the Duwamish. The load of suspended sediment was 1,800 ton/yr (table 30). About 57 percent of the total nitrogen load, or 25 ton/yr, was composed of inorganic nitrogen, so, at 43 percent, organic nitrogen was an important component of the total nitrogen load. For this study, the inorganic nitrogen load was a little lower (by about 20 percent) and the phosphorus load a little higher (by about 15 percent) than the loads estimated for the historical period of 1980-93 (Embrey and Inkpen, 1998). Contrary to the pattern seen in concentration data from the 10 other sites in this study, nutrient concentrations in samples from Springbrook during this study were generally lower than the historical data. Nutrient and suspended-sediment loads transported during fall and winter greatly exceeded summertime loads. In winter, the creek transported an average of 470 lb/d of total nitrogen, 71 lb/d of phosphorus, and 4,400 lb/d of suspended sediment. In response to low flows during summer, the average loads were reduced to 75 lb/d of total nitrogen, 11 lb/d of phosphorus, and 220 lb/d of suspended sediment.

Big Soos transported 200 ton/yr of total nitrogen, 9.5 ton/yr of phosphorus, 2.9 ton/yr of orthophosphate, and 13,000 ton/yr to the Green River (<u>table 30</u>). Seventy-five percent of the nitrogen load, or 150 ton/yr, was composed of inorganic nitrogen. The inorganic nitrogen load of this study was about 30 percent greater than an estimate of 110 ton/yr for the historical period of 1980–93 (Embrey and Inkpen, 1998), and the phosphorus load was about 60 percent greater than the load for the historical period. Above-normal streamflows during 1996 and 1997 resulted in the higher calculations of loads for this 1996–98 study. With higher streamflows in winter, Big Soos transported 2,700 lb/d of total nitrogen, 140 lb/d of phosphorus, and 270,000 lb/d of suspended sediment. Summertime loads fell to 210 lb/d of total nitrogen, 7 lb/d of phosphorus, and 1,700 lb/d of suspended sediment.

Newaukum transported 210 ton/yr of total nitrogen, 27 ton/yr of phosphorus, and 14 ton/yr of orthophosphate to the Green River. The load of suspended sediment amounted to 2,200 ton/yr. The loads were all considerably higher in 1996 and 1997 than in 1998 (table 30). Inorganic nitrogen made up 76 percent (160 ton/yr) of the total nitrogen load. The inorganic nitrogen load of this study was about 30 percent larger than the estimate of 120 ton/yr for the historical period of 1980-93 (Embrey and Inkpen, 1998), and the phosphorus load was a little more than twice the load of 12 ton/yr for the historical period. Concentrations of ammonia and of nitrite-plus-nitrate nitrogen observed during this study were generally similar to the historical data. Fifty percent of phosphorus concentrations in this study were equal to or greater than 0.16 mg/L, whereas, only about 25 percent of the historical data exceeded 0.16 mg/L. The high concentrations and above-normal streamflows resulted in the higher estimates of loads for the 1996–98 period than for the 1980–93 period. In winter, Newaukum transported an average of 2,300 lb/d of total nitrogen, 420 lb/d of phosphorus, and 36,000 lb/d of suspended sediment. With low flow in summer, average loads were reduced to 410 lb/d of total nitrogen, 18 lb/d of phosphorus, and 1,000 lb/d of suspended sediment.

Loads in the headwaters of the Green-Duwamish River Basin at site 10 were about 6 ton/yr of total nitrogen, 0.7 ton/yr of orthophosphate, and 510 ton/yr of suspended sediment (<u>table 30</u>). Using the Beale ratio estimate, the load of phosphorus ranged from 2 to 2.6 ton/yr. Inorganic nitrogen made up 85 percent (5.1 ton/yr) of the total nitrogen load. During winter, the upper Green transported about 38 lb/d of total nitrogen, 4.6 lb/d of orthophosphate, and 3,500 lb/d of suspended sediment. Summertime loads were only 13 lb/d of total nitrogen, 2.1 lb/d of orthophosphate, and 420 lb/d of suspended sediment.

The Green-Duwamish River Basin yielded, per year, an average of 2.8 ton/mi² of total nitrogen, 0.4 ton/mi² of phosphorus, and 0.1 ton/mi² of orthophosphate (<u>fig. 44</u>) to Puget Sound and represented combined nutrient-source loadings to the watershed from human land-use activities and natural processes. Total nitrogen loading each year to the basin from animal manures, agricultural fertilizers, and precipitation was about 4.5 ton/mi² and phosphorus loading was 0.65 ton/mi² (Embrey and Inkpen, 1998). Upstream from site 6 on the Duwamish River, the mainstem received nearly 13 ton/mi² of total nitrogen, 1.5 ton/mi^2 of phosphorus, and 0.6 ton/mi^2 of orthophosphate from the three tributary basins included in this study, Springbrook, Big Soos, and Newaukum. The yields at site 6 indicated dilution of tributary inputs of nutrients, probably by the volumes of high-quality water coming from the upper basin. Annual nutrient yields from Springbrook Creek Basin were 2.2 ton/mi² of total nitrogen, 0.3 ton/mi² of phosphorus, and 0.06 ton/mi² of orthophosphate. Springbrook is primarily an urban basin (72.7 percent of the basin area) with some agriculture (19.8 percent of the basin area), so much of the nutrient-loading sources would be from commercial and residential fertilizer applications, some from agricultural activities, and some from natural sources. Big Soos at site 8 yielded 3.0 ton/mi^2 of total nitrogen, 0.1 ton/mi² of phosphorus, and 0.04 ton/mi^2 of orthophosphate to the Green River. About 50 percent of the Big Soos Creek Basin is urbansuburban, with much of the upper basin in residential and commercial development; 45 percent of the basin is forested and about 2 percent of the basin is agricultural consisting mostly of small farms. Nutrientloading sources would be largely from commercial and residential fertilizer applications, precipitation, and other natural sources. Annual nutrient yields from Newaukum at site 9 was 7.6 ton/mi² of total nitrogen, 1.0 ton/mi² of phosphorus, and 0.5 ton/mi² of orthophosphate. Newaukum is primarily an agricultural basin, partly dairy and beef cattle and partly hobby farms with horses or other animals. Nutrient-loading sources would be mostly animal manures, agricultural fertilizers, and precipitation. The upper Green at site 10 yielded only 0.4 ton/mi² of total nitrogen, approximately 0.1 ton/mi² of phosphorus, and 0.04 ton/mi² of orthophosphate. Land use in the upper Green is a mix of forestry practices and undeveloped, forested terrain. Thus, nutrient source loadings to the upper basin would derive from human activities associated with timber harvest, roads, and recreation, and natural sources such as rock weathering, biological fixation, and precipitation.

Table 30. Loads and basin yields during 1996, 1997, and 1998 and their averages for the study period 1996-98; average loads for the historical period 1980-93; and daily loads, by season, for the study period 1996-98 at site 6, site 7, site 8, site 9, and site 10, Green-Duwamish River Basin, in the Puget Sound Basin study unit, Washington

[-, not calculated; ton/mi², tons per square mile]

			Total	nitroger	n loads a	and yie	lds		Inorganic nit (tons per	•	Total nitrogen load, by season (pounds per day)				
Site name	Year	ly load (to	ons)	Yearly yield (ton/mi ²)			Annual	Annual	For study period	For					
(site No.)	1996	1997	1998	1996	1997	1998	average load for 1996-98 (tons)	average yield for 1996-98 (ton/mi ²)	1996-98 (Percentage of total nitrogen load)	historical period 1980-93	Winter	Spring	Summer	Fall	
Duwamish River (6)	1,500	1,400	840	3.2	3.0	1.8	1,300	2.8	860 (66)	520	15,000	6,900	1,700	4,400	
Springbrook Creek (7)	52	47	33	2.6	2.4	1.6	44	2.2	25 (57)	31	470	230	75	200	
Big Soos Creek (8)	240	240	120	3.6	3.6	1.8	200	3.0	150 (75)	110	2,700	1,100	210	520	
Newaukum Creek (9)	230	250	150	8.4	9.1	5.5	210	7.6	160 (76)	120	2,300	1,200	410	680	
Green River (10)	7.0	7.1	4.0	0.42	0.43	0.24	6.0	0.37	5.1 (85)	_	38	54	13	27	

					Phosp	horus lo	ads and yield	S		Phosphorus loads, by season (pounds per day)					
Site name (site	Yearl	y load (tons)	Yearly yield (ton/mi ²)			Annual	Annual	Annual average						
No.)	1996	1997	1998	1996	1997	1998	average load for 1996-98 (tons)	average yield for 1996-98 (ton/mi ²)	load for the historical period 1980-93 (tons)	Winter	Spring	Summer	Fall		
Duwamish River (6)	290	200	75	0.63	0.43	0.16	190	0.4	89	2,300	880	200	720		
Springbrook Creek (7)	7.6	7.4	5.6	.38	.37	.28	6.9	.34	5.9	71	37	11	32		
Big Soos Creek (8)	12	12	4.6	.18	.18	.07	9.5	.14	6.2	140	50	7.0	16		
Newaukum Creek (9)	42	29	10	1.5	1.1	.36	27	.98	12	420	90	18	63		
Green River (10)	-	-	-	_	-	_	2-2.6	.1216	_	_	_	_	-		

Table 30. Loads and basin yields during 1996, 1997, and 1998 and their averages for the study period 1996-98; average loads for the historical period 1980-93; and daily loads, by season, for the study period 1996-98 at site 6, site 7, site 8, site 9, and site 10, Green-Duwamish River Basin, in the Puget Sound Basin study unit, Washington—*Continued*

			0	rthopho	sphate p	hosphori	ıs loads and	yields		Orthophosphate phosphorus loads, by season (pounds per day)					
Site name	Year	ly load (1	tons)	Yearly yield (ton/mi ²)			Annual	Annual	Annual average						
(site No.)	1996	1997	1998	1996	1997	1998	average load for 1996-98 (tons)	average yield for 1996-98 (ton/mi ²)	load for the historical period 1980- 93 (tons)	Winter	Spring	Summer	Fall		
Duwamish River (6)	55	51	28	0.12	0.11	0.06	44	0.1	46	450	250	87	190		
Springbrook Creek (7)	1.5	1.4	1.0	.08	.07	.05	1.3	.06	-	12	9.0	3.0	5.0		
Big Soos Creek (8)	3.0	3.4	2.4	.04	.05	.04	2.9	.04	2.2	33	14	5.0	12		
Newaukum Creek (9)	19	16	7.2	.69	.58	.26	14	.51	7	190	61	16	39		
Green River (10)	0.8	0.8	0.6	.05	.05	.04	0.7	.04	_	4.6	6.0	2.1	3.1		

			Susp	ended-s	edimer	ıt loads a	and yields			Suspended-sediment loads, by season, (pounds per day)					
Site name	Year	ly load (ton	is)	Yearly yield (ton/mi ²)			Annual	Annual	Annual average						
(site No.) Duwamish	1996	1997	1998	1996	1997	1998	average load for 1996-98 (tons)	average yield for 1996-98 (ton/mi ²)	load for the historical period 1980-93 (tons)	Winter	Spring	Summer	Fall		
Duwamish River (6)	500,000	240,000	59,000	1,100	520	130	270,000	580	_	3,900,000	970,000	120,000	970,000		
Springbrook Creek (7)	2,400	1,900	1,000	120	95	50	1,800	88	-	24,000	7,000	1,200	6,900		
Big Soos Creek (8)	23,000	14,000	2,400	340	210	36	13,000	200	-	250,000	35,000	1,700	9,300		
Newaukum Creek (9)	3,600	2,300	810	95	84	30	2,200	81	-	36,000	9,000	1,000	3,200		
Green River (10)	900	480	150	55	29	9	510	31	_	3,500	3,600	420	3,700		

Thornton Creek Basin

During the period 1997–98, the urban stream Thornton Creek transported 20 ton/yr of total nitrogen, 1.5 ton/yr of phosphorus, 0.4 ton/yr of orthophosphate, and 530 ton/yr of suspended sediment to Lake Washington (table 31). Seventy percent of the total nitrogen load, or 14 ton/yr, was composed of inorganic nitrogen; at 30 percent, organic nitrogen was an important component of the total nitrogen load. The inorganic nitrogen load of 14 ton/yr for this study was essentially the same as the estimate of 15 ton/yr for the historical period of 1980-93 (Embrey and Inkpen, 1998); the phosphorus load for the historical period was estimated at 1 ton/yr, which was a little less than the estimate for the 1997–98 study period. Ammonia and phosphorus concentrations in about 10 percent of the samples collected during this study were higher than concentrations in the historical data; nitrite-plusnitrate concentrations, however, were similar to the

historical data. The higher load estimates in this study might in part result from using different methods to calculate loads; but the above-normal streamflows during this study would result in higher loads than those for the historical period of 1980–93. In winter, Thornton transported an average of 160 lb/d of total nitrogen, 12 lb/d of phosphorus, and 6,700 lb/d of suspended sediment. In summer, with lower streamflows, average loads dropped to 52 lb/d of total nitrogen, 3 lb/d of phosphorus, and 360 lb/d of suspended sediment.

The annual total nitrogen yield from Thornton Creek Basin was 1.6 ton/mi² (fig. 43 and 44), the annual phosphorus yield was 0.1 ton/mi², and the orthophosphate yield was 0.03 ton/mi². Thornton is a fully developed urban basin, thus nutrient loading sources would mostly come from commercial and residential fertilizer applications, precipitation, and natural sources.

 Table 31.
 Loads and basin yields during 1996, 1997, and 1998 and their averages for the study period 1996-98; average loads for the historical period

 1980-93; and daily loads, by season, for the study period 1996-98 at site 11, Thornton Creek Basin, in the Puget Sound Basin study unit, Washington

Site name (site No.)			Total	nitroge	ı loads	and yie	lds		Inorganic niti (tons per	•	Total nitrogen load, by season (pounds per day)			
	Year	ly load (t	tons)	Yearly	Yearly yield (ton/mi ²)			Annual	For study	-				
	1996	1997	1998	1996	1997	1998	average load for 1996-98 (tons)	average yield for 1996-98 (ton/mi ²)	period 1996-98 (Percentage of total nitrogen load)	For historical period 1980-93	Winter	Spring	Summer	Fall
Thornton Creek (11)	_	22	17	-	1.8	1.4	20	1.6	14 (70)	15	160	130	53	85

Site name (site No.)					Phos	phorus la	ads and yield	s		Phosphorus loads, by season (pounds per day)					
	Year	y load (tons)	Yearly yield (ton/mi ²)			Annual	Annual	Annual average						
	1996	1997	1998	1996	1997	1998	average load for 1996-98 (tons)	average yield for 1996-98 (ton/mi ²)	load for the historical period 1980-93 (tons)	Winter	Spring	Summer	Fall		
Thornton Creek (11)	-	1.9	1.0	-	0.16	0.08	1.5	0.12	1	12	11	3.0	6.0		

Table 31.Loads and basin yields during 1996, 1997, and 1998 and their averages for the study period 1996-98; average loads for the historical period1980-93; and daily loads, by season, for the study period 1996-98 at site 11, Thornton Creek Basin, in the Puget Sound Basin study unit, Washington—
 Continued

Site name (site No.)			Ortho	phospha		Orthophosphate phosphorus loads, by season (pounds per day)							
	Yearly load (tons) 1996 1997 1998			Yearly 1996	Yearly yield (ton/mi ²) 1996 1997 1998			Annual average yield for 1996-98 (ton/mi ²)	Annual average load for the historical period 1980-93	Winter	Spring	Summer	Fall
Thornton Creek (11)	_	0.4	0.3	_	0.03	0.02	0.4	0.03	(tons) 0.6	2.5	2.1	1.5	2.3

Site name (site No.)			Susp	ended-so	ediment	loads ar	ıd yields			Suspended-sediment loads, by season, (pounds per day)				
	Yea	Yearly yield (ton/mi ²)					Annual							
	1996	1997	1998	1996	1997	1998	Annual average load for 1996-98 (tons)	Annual average yield for 1996-98 (ton/mi ²)	average load for the historical period 1980-93 (tons)	Winter	Spring	Summer	Fall	
Thornton Creek (11)	_	680	380	_	56	31	530	44	_	5,500	3,200	800	2,200	

TRENDS IN CONCENTRATIONS OF NITRATE AND TOTAL PHOSPHORUS

The seasonal Kendall test (Crawford and others, 1983) was applied to data collected by Washington State Department of Ecology and King County to determine the trend in nitrate and total phosphorus concentrations over time at six sites in the PSB. Five of these sites were sampled during this study and one, Green River at Renton Junction, is 2 river miles upstream from site 6 of this study, the Duwamish River. The new site was included because it was the only station on the Green with an extensive period of record. For four sites, the seasonal Kendall test was performed on nitrate and total phosphorus concentrations for water years 1980–97. For the Skokomish River, the test was performed for water years 1984–97; for the Green River at Renton Junction, it was performed on nitrate concentrations for water years 1980-97 and on total phosphorus concentrations for calendar year 1981 through water year 1997. The analytical method for total phosphorus changed at the beginning of 1981 (Robert Brenner, City of Seattle Metropolitan Services, written commun., 1999), so total phosphorus data collected at sites in the Green River Basin prior to 1981 were not included in the trend tests. Streamflow data were obtained at on-site or nearby gages. For the Green River at Renton Junction, Nooksack River at North Cedarville, and the Nooksack River at Brennan, streamflow data were from gaging stations located at Green River at Auburn, Nooksack River at Deming, and Nooksack River at Ferndale, respectively.

The seasonal Kendall test is a nonparametric test that compares the relative ranks of the data rather than the actual concentration values. Because monthly data were available, the seasons were defined to be the 12 months; therefore, only January data are compared with January data, and so forth for the rest of the months. If more than one sample was collected during a month, the median value was used. All possible pairs of monthly data are compared in the test. If a value later in time is higher, then a plus is recorded; if a value later in time is lower, then a minus is recorded. If an upward trend is present, there will be many more pluses than minuses. If no trend is present, then the numbers of pluses and minuses are about equal. Because the seasonal Kendall test uses ranks instead of concentration values, it easily handles censored values

(below method reporting levels), which were set to half of the lowest censored concentration (Crawford and others, 1983).

The seasonal Kendall test was performed on both unadjusted and flow-adjusted concentrations. The locally weighted scatterplot smoothing (LOWESS) technique (Cleveland, 1979) was used to help remove changes in concentrations caused by streamflow. The LOWESS procedure fits a curve to scatterplots of constituent concentrations and streamflows measured at the time of sampling. To compute flow-adjusted concentration, the residual between the observed value and the value predicted by the fitted curve is added to the mean constituent concentration. Negative numbers sometime result because the flow-adjusted concentrations are the sum of the regression residual and the mean concentration.

A trend was considered to be statistically significant if the p-value from the seasonal Kendall test was less than or equal to 0.10. The p-values were adjusted for serial correlation (Hirsch and Slack, 1984); however, keeping the number of seasons relatively small, such as the selection of 12 seasons, helps to reduce problems caused by serial correlation (Crawford and others, 1983). Scatterplots for both unadjusted and flow-adjusted concentrations for nitrate and total phosphorus are shown in <u>figures 46</u> through 51 for all data from 1970 to 1998. The LOWESS curves are shown to help identify trends in the concentrations.

Overall, nitrate and total phosphorus concentrations were mostly stable (<u>table 32</u>). No downward trends were detected. Significant upward trends in nitrate concentrations were detected at three of the six sites. Total phosphorus concentrations showed an upward trend only at Newaukum. However, these trend results should be used with caution. According to Hopkins (1993), false or misleading trends can appear especially if concentrations are near the method detection limits.

The Skokomish had a significant upward trend in nitrate concentration for both unadjusted and flow-adjusted data between 1984 and 1997; however, the concentrations appear to have leveled off since the mid-1990's (fig. 46). The trend test indicates, as measured by the slope, that the flow-adjusted nitrate concentrations increased by 0.0036 mg/L per year.

A significant upward trend in nitrate concentrations was also found by Hopkins (1993), who analyzed data from 1979 to 1991. Hopkins also found a significant upward trend in total phosphorus concentrations, but no trends in either flow-adjusted or unadjusted total phosphorus concentrations were found in this study, which might indicate that total phosphorus concentrations have leveled off since the early 1980's.

In the Nooksack River Basin, there were no trends in unadjusted or flow-adjusted concentrations of nitrate or total phosphorus at either of the two sites. Nitrate concentrations at the lower Nooksack River appear to have increased slightly from the early 1970's until about 1987, but have since leveled off (fig. 47). Total phosphorus concentrations at both Nooksack River sites, as well as the nitrate concentrations at the upper Nooksack River have remained fairly level since the 1970's (fig. 47 and 48). Hopkins (1993) also did not find any trends in either nitrate or total phosphorus concentrations at the lower Nooksack River between 1979 and 1991.

In the Green River Basin, there were no trends in nitrate or total phosphorus concentrations for either flow-adjusted or unadjusted data for the Green River at Renton Junction (fig. 49). The steep downward change in total phosphorus concentrations during the 1970's (data that were not used in the trend analysis) at the Green River at Renton Junction is believed to result from using a different analytical method (Robert Brenner, City of Seattle Metropolitan Services, oral commun., 1999). There were, however, significant upward trends in both flow-adjusted and unadjusted nitrate concentrations for Big Soos (fig. 50) and Newaukum (fig. 51) Creeks. As indicated by the trend test slope (rate of change, table 32), flow-adjusted nitrate concentrations for Big Soos showed an increase of 0.01 mg/L per year, and for Newaukum, a slightly larger increase of 0.014 mg/L per year. Additionally, both unadjusted and flow-adjusted total phosphorus concentrations in Newaukum showed a significant upward trend, whereas Big Soos had no significant trends. The increase in flow-adjusted total phosphorus concentrations at Newaukum was about 0.002 mg/L per year. Although nitrate and total phosphorus concentrations for Big Soos and Newaukum had upward trends between 1980 and 1997, it appears that the trends might be reversing with decreasing concentrations beginning in the mid-1990's.

Table 32. Summary of results from seasonal Kendall tests for temporal trends in nitrate nitrogen and total phosphorus concentrations at six surface-water sites in the Puget Sound Basin study unit, Washington

[UP, statistically significant upward trend; NT, no trend; p-value from the Seasonal Kendall test; trend is considered significant if p-value is less than or equal to 0.1; Nitrate, nitrite plus nitrate nitrogen; mg/L, milligrams per liter; <, less than; –, no value; Ecology, Washington State Department of Ecology]

					Tren	ds				- Source of
			Unadjusted fo	or streamflow			Adjusted for	r streamflow		
Site name	Period of analysis	Nitrate (p-value)	Rate of change (mg/L per year)	Total phos- phorus (p-value)	Rate of change (mg/L per year)	Nitrate (p-value)	Rate of change (mg/L per year)	Total phos- phorus (p-value)	Rate of change (mg/L per year)	data (agency)
Skokomish River near	1984-97	UP	0.0033	NT	-	UP	0.0036	NT	_	Ecology
Potlatch		(<0.01)		(0.21)		(<0.01)		(0.21)		
Nooksack River at	1980-97	NT	-	NT	-	NT	-	NT	-	Ecology
Brennan		(.46)		(.43)		(.11)		(.21)		
Nooksack River at	1980-97	NT	-	NT	-	NT	-	NT	_	Ecology
North Cedarville		(.14)		(.63)		(.18)		(.35)		
Green River at Renton	1980-97 ¹	NT	_	NT	_	NT	_	NT	_	King
Junction		(.34)		(.87)		(.29)		(.47)		County
Big Soos Creek near	1980-97	UP	.0127	NT	_	UP	.01	NT	_	King
Auburn		(.01)		(.36)		(.03)		(.50)		County
Newaukum Creek near	1980-97	UP	.0124	UP	0.0018	UP	.0142	UP	0.0017	King
Black Diamond		(.05)		(.01)		(.04)		(<.01)		County

¹ Seasonal Kendall test performed for calendar year 1981 through water year 1997 for total phosphorus.

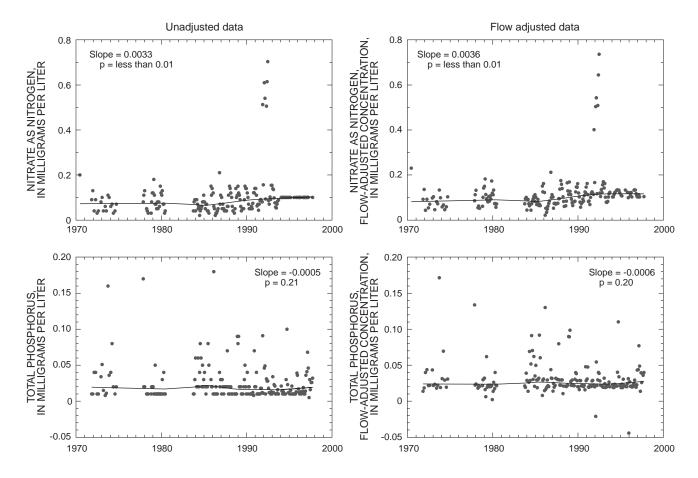


Figure 46. Temporal variations in unadjusted and flow-adjusted concentrations of nitrate and total phosphorus and LOWESS-trend curves for the Skokomish River near Potlatch, in the Puget Sound Basin study unit, Washington.

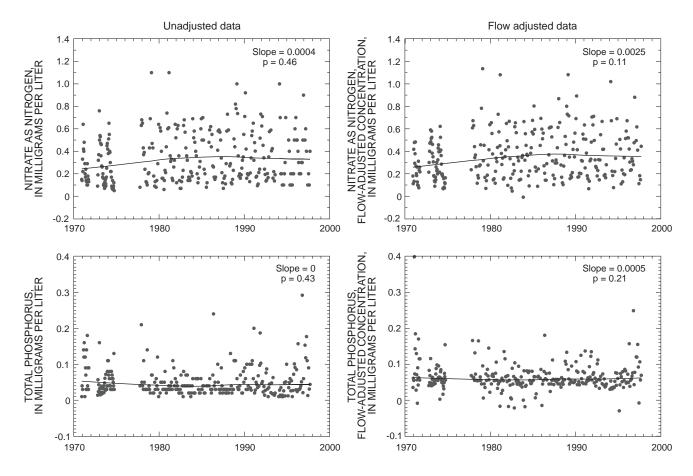


Figure 47. Temporal variations in unadjusted and flow-adjusted concentrations of nitrate and total phosphorus and LOWESS-trend curves for the Nooksack River at Brennan, in the Puget Sound Basin study unit, Washington.

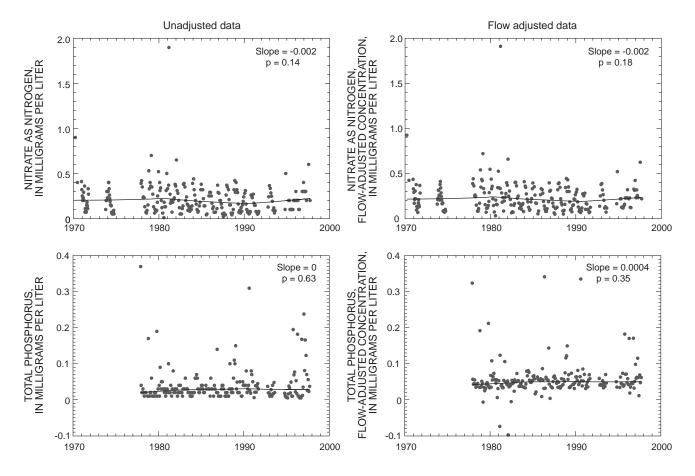


Figure 48. Temporal variations in unadjusted and flow-adjusted concentrations of nitrate and total phosphorus and LOWESS-trend curves for the Nooksack River at North Cedarville, in the Puget Sound Basin study unit, Washington.

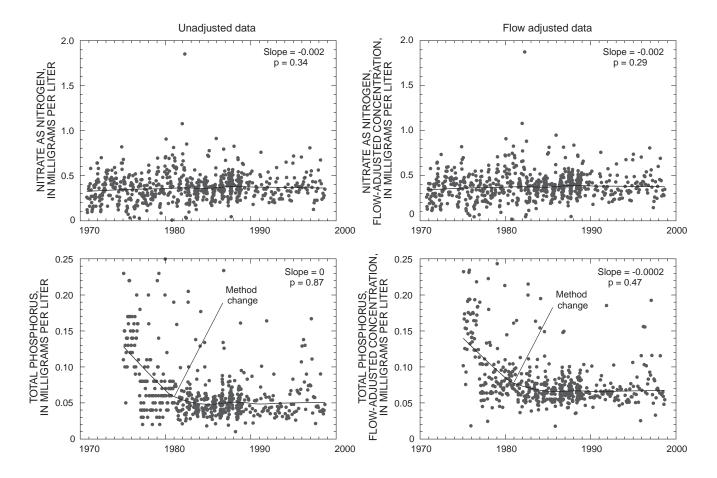


Figure 49. Temporal variations in unadjusted and flow-adjusted concentrations of nitrate and total phosphorus and LOWESS-trend curves for the Green River at Renton Junction, in the Puget Sound Basin study unit, Washington.

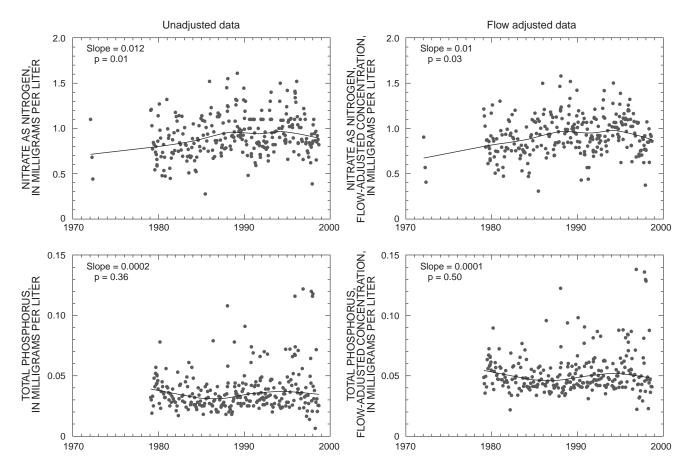


Figure 50. Temporal variations in unadjusted and flow-adjusted concentrations of nitrate and total phosphorus and LOWESS-trend curves for Big Soos Creek above Hatchery near Auburn, in the Puget Sound Basin study unit, Washington.

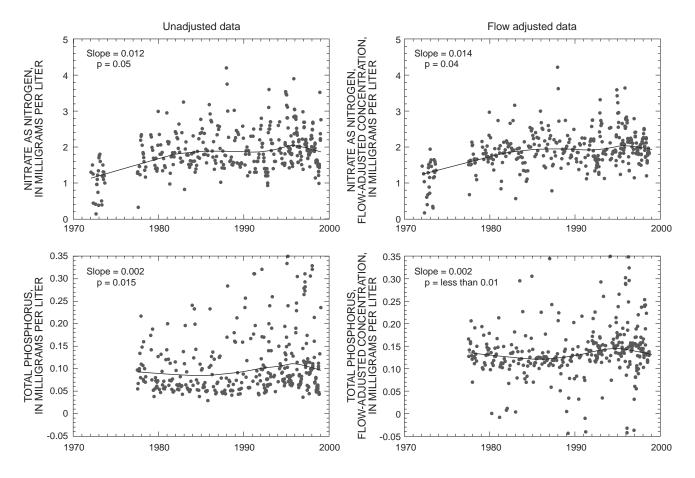


Figure 51. Temporal variations in unadjusted and flow-adjusted concentrations of nitrate and total phosphorus and LOWESS-trend curves for Newaukum Creek near Black Diamond, in the Puget Sound Basin study unit, Washington.

SUMMARY

The Puget Sound Basin study unit team collected streamflow and water-quality data from November 1995 through April 1998 (water years 1996–98) from a fixed-site surface-water network consisting of 11 sites in western Washington. Water samples for analyses of nutrients, major ions, organic carbon, and suspended sediment and measurements of physical properties were collected monthly, with additional sampling during storm-runoff and high-flow events. The fixedsite network was established in three major river basins—the Skokomish River Basin with two sites, the Nooksack River Basin with three sites, and the Green-Duwamish River Basin with five sites—and in one small urban basin, the Thornton Creek Basin with one site.

Three of the 11 sites—Skokomish River near Potlatch, Nooksack River at Brennan (lower Nooksack), and Duwamish River at Tukwila-are integrators of mixed land uses. The sites are located near the mouths of their respective basins and are locally influenced by forestry practices, agriculture, and urbanization, respectively. The remaining eight sites are indicators of relatively homogeneous land useland cover in their basins. Seven of the indicator sites are on tributaries within the three major river basins and one is on Thornton Creek, a small stream draining into Lake Washington. The site on the North Fork (NF) Skokomish is an indicator site representing reference or background conditions in the study unit. In the Nooksack River Basin, the site on Fishtrap Creek is an indicator site representing an intensively farmed tributary basin with some urban influences from part of the basin in Canada and the city of Lynden, and the site on the Nooksack River at North Cedarville (upper Nooksack) is an indicator site of forest practices in the upper basin. In the Green-Duwamish River Basin, four sites, one on each of four tributaries, are indicators of conditions typical of urban-suburban settings in the study unit: Springbrook Creek, of commercial and light industrial land use; Big Soos Creek, of an urbanizing basin; Newaukum Creek, of agriculture that includes cattle, horse, and hobby farms; and the upper Green River, of forest practices as well as the conditions in basins with headwaters in the mountains. Thornton is an indicator of long-established, high-density residential and commercial development.

Sampling conditions during the first 18 months of the study were wet and dominated by above-normal precipitation. Water year 1997 was the wettest of the 3 years in the study period. Nearly 52 inches of precipitation fell (about 14 inches above average); monthly precipitation was often 200 percent of normal. The wet years caused many runoff events and flooding, keeping streamflows generally above median values and contributing to high concentrations of nutrients, suspended sediment, and organic carbon, and to detectable concentrations of several volatile organic compounds (VOCs) and pesticides.

Water in the Skokomish at site 1 was of generally high quality, although suspended-sediment concentrations were occasionally high, with a maximum of 1,470 mg/L (milligrams per liter). In 2 of the 37 samples collected, iron concentrations of as much as 430 μ g/L (micrograms per liter) exceeded the U.S. Environmental Protection Agency (USEPA) secondary maximum contaminant level (SMCL) of 300 μ g/L for drinking water. Skokomish water was chemically dilute, with a median dissolved-solids concentration of 41 mg/L. Nutrient concentrations were also low, with at least half of the organic nitrogen, nitrite, and dissolved-phosphorus concentrations below laboratory minimum reporting levels (MRLs), and a median nitrate concentration of 0.09 mg/L.

The water at site 2 on the NF Skokomish was of exceptionally high quality. Unlike site 1, suspended-sediment and iron concentrations in samples were low. Out of 33 samples, the maximum suspended-sediment concentration observed was 122 mg/L and iron concentrations were equal to or less than 25 μ g/L. The water was chemically dilute, with a median dissolved-solids concentration of 45 mg/L. Concentrations of nutrients were also low, with at least half of the total and dissolved organic nitrogen, nitrite, total and dissolved phosphorus, and orthophosphate concentrations below laboratory MRLs and a median nitrate concentration of 0.05 mg/L.

The water in the lower Nooksack River (site 3) was of generally good quality except for a few occasions when suspended-sediment concentrations were relatively large and a number of pesticides and VOCs were detected. Ten percent of the 41 samples had suspended-sediment concentrations greater than 1,500 mg/L and the maximum was 2,890 mg/L. The water was chemically dilute, with a median dissolved-solids concentration of 57.5 mg/L.

Concentrations of nutrients were moderate, with about 10 percent of the ammonia, nitrite, total and dissolved phosphorus, and orthophosphate concentrations below laboratory MRLs and a median nitrate concentration of 0.35 mg/L.

Fishtrap Creek (site 4), where 44 samples were collected, had water of fair quality except when iron and manganese concentrations were large and a number of pesticides and VOCs were detected. In 8 of 14 samples collected from April 1997–August 1998, concentrations of *Escherichia coli* exceeded 298 col/100mLs (colonies per 100 milliliters), USEPA's recommended single-sample level for moderate, fullbody contact recreation. Occasionally, concentrations of iron and manganese did not meet USEPA SMCLs for drinking water. Dissolved solids, with a median concentration of 151 mg/L, were moderately high. All forms of nitrogen analyzed were present in nearly all samples, and nitrate, with a median concentration of 2.8 mg/L, was the dominant nitrogen species.

Thirty-five water samples from the upper Nooksack River at site 5 indicated the water was of generally high quality except for occasionally high suspended-sediment concentrations. Ten percent of the samples had suspended-sediment concentrations greater than 1,900 mg/L and the maximum observed was 3,210 mg/L. The water was chemically dilute, as indicated by dissolved solids with a median concentration of 49 mg/L. Concentrations of nutrients were also low, with at least half of the organic nitrogen, nitrite, dissolved phosphorus, and orthophosphate concentrations below laboratory MRLs. The median nitrate concentration was 0.21 mg/L.

Forty-two water samples were collected from the Duwamish River at site 6. Occasionally, iron and manganese concentrations were large and a number of pesticides and VOCs were detected. Ten percent of the samples had iron and manganese concentrations greater than 400 and 70 μ g/L, respectively, exceeding USEPA SMCLs for drinking water. The water was chemically dilute, with a median dissolved-solids concentration of 62 mg/L. Concentrations of nutrients were moderately low, with at least 10 percent of the concentrations of reduced forms of nitrogen and of dissolved phosphorus and orthophosphate below laboratory MRLs. Nitrate, with a median concentration of 0.41 mg/L, and total organic nitrogen with a median of 0.20 mg/L, were the most prevalent nitrogen species.

Thirty-seven water samples were collected from Springbrook Creek (site 7); two of these samples, collected during storm runoff in October 1996, were analyzed for pesticides and VOCs. The water in Springbrook was of fair quality. In 25 of the 37 samples, dissolved-oxygen concentration measured at the time of collection did not meet the Washington State standard of 8.0 mg/L for a Class A water body. The water was moderately high in dissolved solids, with a median concentration of 152 mg/L, and major ions. Concentrations of nutrients were moderately high, with more than 90 percent of the ammonia, dissolved phosphorus, and orthophosphate concentrations above laboratory MRLs and a median nitrate concentration of 0.43 mg/L.

A total of 36 samples indicated the water in Big Soos Creek at site 8 to be of good quality. Concentrations of *Escherichia coli* were sometimes large, ranging from 21 to 750 col/100mLs. Of eight samples collected, two had concentrations that exceeded 298 col/100mLs, USEPA's recommended single-sample level for moderate, full-body contact recreation. The water was moderately low in dissolved solids, with a median concentration of 84 mg/L. Concentrations of nutrients were also moderately low, with most ammonia, nitrite, total organic nitrogen, and dissolved phosphorus concentrations below laboratory MRLs and a median nitrate concentration of 0.875 mg/L.

On the basis of 36 samples, the water in Newaukum Creek at site 9 was of moderately good quality with respect to water temperatures, dissolvedoxygen concentrations, and pH levels that were within Washington State standards for a Class A water body. In a sample collected on August 4, 1998, concentrations of fecal-coliform bacteria exceeded the State's standard of 100 col/100mLs for a Class A water body and enterococci bacteria exceeded 89 col/100mLs, USEPA's recommended single-sample level for moderate, full-body contact recreation. The water was moderately low in dissolved solids, with a median concentration of 107 mg/L. The creek, however, was rich in nutrients relative to other sites in this study. Nitrate concentrations were second-highest after Fishtrap and total phosphorus concentrations were second-highest after Springbrook. Seventy-five percent of ammonia and organic nitrogen concentrations and 90 percent of phosphorus and orthophosphate concentrations were above the laboratory MRLs.

The water in the upper Green River at site 10 was of high quality, similar to that of the study's reference site on the NF Skokomish. The water was chemically dilute, as indicated by a median dissolved-solids concentration of 36 mg/L. Concentrations of nutrients were also low; nitrate was detected in only 38 percent of the samples, with a median concentration of 0.04 mg/L. In a single sample collected during a runoff event in October 1997, the suspended-sediment concentration was 243 mg/L, the maximum observed for this site; however, 90 percent of the 24 samples collected had suspended-sediment concentrations less than 15 mg/L. Also in this October sample, the maximum observed iron concentration of 520 µg/L exceeded the USEPA SMCL for drinking water.

Water in Thornton Creek (site 11) was of fair quality. Out of 46 samples, iron and manganese concentrations were occasionally large and a number of pesticides and VOCs were detected. Concentrations of Escherichia coli in 9 of 14 samples exceeded 298 col/100mLs, USEPA's recommended singlesample level for moderate, full-body contact recreation. The water had moderately high concentrations of dissolved solids, with a median concentration of 150 mg/L, and was moderately rich in nutrients relative to the other sites in this study. All the forms of phosphorus analyzed were detected above MRLs in at least 89 percent of the samples. All forms of nitrogen analyzed were also detected in most of the samples; however, nitrate, with a median concentration of 1.26 mg/L was the dominant nitrogen species.

Several pesticides, most of them herbicides, and VOCs, mostly fuel-related, solvent-related, or halogenated, were detected in water samples collected from the lower Nooksack River, Fishtrap Creek, the Duwamish River, and Thornton Creek. Pesticide and VOC concentrations tended to be higher and detections more frequent during the wet season from about November through March. Maximum pesticide concentrations often were in storm-runoff samples, which usually coincided with the spring season when many compounds are typically applied. But concentrations could also be high in runoff samples during summer and early fall. Except as noted below, no pesticide or VOC concentrations exceeded existing or applicable water-quality standards or criteria concentrations.

In the lower Nooksack River, 16 pesticides were detected. Atrazine was detected most often, in 15 of 22 samples, in concentrations up to $0.42 \mu g/L$ and with a

median of $0.016 \mu g/L$. Fifteen VOCs were detected in samples; however, only methylbenzene was detected at concentrations above the 1999 laboratory reporting level (LRL).

In Fishtrap, 29 pesticides were detected, nearly twice the number detected downstream in the lower Nooksack. The herbicides atrazine, simazine, and the transformation product deethylatrazine were detected in 31 of 32 samples. Seven insecticides-carbaryl, carbofuran, diazinon, ethoprophos, malathion, oxamyl, and propargite-were also detected. Diazinon concentrations in five samples, and carbaryl concentrations in three samples, did not meet recommended aquatic-life criteria. Eighteen VOCs were detected. Chloromethane was most frequently detected, in 22 of 32 samples, but all detections were below the 1999 LRL. Of six compounds (chlorobenzene, ethylbenzene, dichloromethane, methylbenzene, 1,3-plus-1,4-dimethylbenzene, and 1,2-dimethylbenzene) detected at concentrations above the 1999 LRLs, methylbenzene was detected most frequently (53 percent of samples).

Thirteen pesticides were found in 24 samples from the Duwamish River. Simazine, prometon, atrazine, and tebuthiuron were the most frequently detected pesticides. Diazinon was the only insecticide detected and was found in eight samples in concentrations as high as 0.083 μ g/L. Diazinon concentrations in two samples exceeded 0.04 μ g/L, a level recommended for the protection of aquatic life. Twenty-six VOCs were detected; however, only two (methylbenzene and 1,3-plus-1,4-dimethylbenzene) were detected at concentrations above the 1999 LRLs.

In Thornton Creek, 21 pesticides were detected, and again, most of these were herbicides. Prometon was detected most frequently, in nearly 100 percent of the 46 samples. Of the herbicides, simazine and dichlobenil were the next most frequently detected, found in 23 and 21 samples, respectively. Five insecticides-carbaryl, chlorpyrifos, diazinon, lindane, and malathion, were also detected. Diazinon was detected in 85 percent of the samples, 15 of which had concentrations exceeding 0.04 µg/L, a limit recommended for the protection of aquatic life. Diazinon was also the insecticide purchased at the highest rate by the public through retail outlets in King County. Two sample concentrations of carbaryl, one of chlorpyrifos, and one of lindane also exceeded limits recommended for the protection of aquatic life.

In urban streams such as Thornton Creek, insecticides typically used on residential lawns and gardens have increased the frequency of detections and concentrations that do not meet criteria. In samples from Thornton, 32 VOCs were detected, the most of all four sites sampled for VOCs. Ten compounds (acetone, bromoform, trichloromethane, ethylbenzene, dichloromethane, 4-methyl-2-pentanone, methylbenzene, 1,2-dimethylbenzene, 1,3-plus-1,4dimethylbenzene, and 1,2,4-trimethylbenzene) were detected at concentrations above the 1999 LRLs. More than 70 percent of methylbenzene detections were in concentrations above the LRL, the most of any site.

Water-quality conditions at the study sites resulted from both natural characteristics of the watersheds and human activities. In the Nooksack and Skokomish Rivers, natural conditions probably contributed, in part, to the large suspended-sediment concentrations observed during high streamflow events. However, logging and road building in the basins might also have contributed to the suspendedsediment loads. In the forested study basins, dissolved solids and nutrient concentrations were low. At the reference site on the NF Skokomish and the forestry practices indicator site on the upper Green, natural conditions were reflected in high-quality water with low concentrations of dissolved solids, nutrients, and suspended sediment, and standards or criteria that were nearly always met. Unlike the high-quality water at the reference and forestry sites, natural conditions appear to have adversely affected the quality of water in Springbrook Creek. High concentrations of iron and manganese and low dissolved-oxygen concentrations were possibly the result of ground-water discharge to this tributary.

Of all the sites, nutrient concentrations were highest in the agricultural streams (Fishtrap and Newaukum Creeks) and next highest in the urban streams (Springbrook, Big Soos, and Thornton Creeks), largely because of human activities. Of the three large rivers integrating a mix of land uses, the lower Nooksack (in an agricultural setting) had on average, the highest total nitrogen and phosphorus concentrations, followed by the Duwamish (in an urban setting) and the Skokomish (in a forestry practices setting). An earlier study showed that fertilizer applications to lands within the study unit corresponded to nitrogen concentrations and yields from the major river basins. Nutrient loads transported in the surface water at the 11 sites during this study ranged from 6.0 to 3,200 tons per year of total nitrogen in the upper Green and the lower Nooksack, respectively, and from about 2 to 890 tons per year of total phosphorus in the upper Green and the lower Nooksack, respectively.

Of the three major river basins of this study, nutrient yields were largest from the Nooksack River Basin and smallest from the Skokomish River Basin. The Nooksack River Basin was estimated to have one of the highest source loading rates among the major Puget Sound Basin watersheds, receiving 9.1 tons of nitrogen and 1.3 tons of phosphorus per square mile of drainage, whereas the Skokomish River Basin had one of the lowest rates, receiving 0.4 ton of nitrogen and 0.2 ton of phosphorus per square mile of drainage. From Fishtrap and Newaukum Creeks, total nitrogen yields of 8.8 and 7.7 tons per square mile, respectively, were the highest of the 11 sites. Yields from the urban and suburban basins also were well above those from the reference and forestry basins. From Big Soos Creek, the total nitrogen yield of 3.0 tons per square mile was the highest of the urban streams.

Pesticides affected water quality at the four sites where they were measured, whether the site was in an urban or agricultural setting. More types of pesticides were detected in samples from the agricultural sites than from the urban sites. The most pesticides were detected in Fishtrap Creek. Many pesticides were those applied for agricultural purposes, but several were pesticides typically applied in urban settings, such as those used in maintaining rights-of-way. Although more types of pesticides were detected in samples from agricultural streams, pesticides were applied in larger quantities in the urban areas. In the 1980's, about 18 percent of the total herbicide and 31 percent of the total insecticide applications in the study unit were to King County, where Thornton Creek and the Duwamish River are located. About 9 percent of the herbicide and 3 percent of the agricultural and nonagricultural applications of insecticides were to Whatcom County, where Fishtrap Creek and the Nooksack River are located.

The generally higher concentrations, the detections of certain pesticides in samples year round, and the number of times insecticide concentrations did not meet aquatic-life criteria in Thornton were at least partly because of these high application rates and availability of pesticides in urban areas.

More VOCs were detected, and at a higher detection frequency, at the two sites in urban areas than at the two sites in agricultural areas. The most compounds were detected, and in the highest concentrations, at Thornton. Conversely, the least number of compounds were detected in lower Nooksack, with only 2 percent urban land upstream. Many VOCs detected in samples from all four sites were fuel related. MTBE, an automotive fuel additive used in Canada, was detected in a few samples from Fishtrap. Many solvents were also detected, particularly in samples from the Duwamish and Thornton. Carbon disulfide, chloromethane, and 4methyl-2-pentanone were the most commonly detected solvents. Other solvents, such as trichloroethene (TCE) and tetrachloroethene (PCE), were detected only in samples from the urban sites. The only VOC with a distinctly agricultural signature was 1,2dichloropropane, detected only in Fishtrap Creek samples. 1,2-dichloropropane was historically used as a soil fumigant and, at the time of this study, was present in trace amounts in formulations of 1,3dichloropropene, which was still applied in the Washington State part of Fishtrap Creek Basin.

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Table 33. Fecal-indicator bacteria and coliphage in samples collected at selected surface-water sites in the Puget Sound Basin study unit, Washington

[Abbreviations: col/100ml, colonies per 100 milliliters; pfu/100ml; plaque-forming units per 100 milliliters; <, less than; ^K, estimate based on non-ideal count; -, no data]

Date	Total coliform, col/100mL	Fecal coliform, col/100mL	<i>Escherichia coli,</i> col/100mL	Enterococcus, col/100mL	<i>Clostridium perfringens,</i> col/100mL	Somatic coliphage, pfu/100mL	Male-specific coliphage, pfu/100mL
Thornton Creek nea		0, site 1					
19970407	720	_	^K 250	_	-	-	_
19970505	1,600	-	170	-	-	-	_
19970520	26,000	-	^K 9,600	_	_	-	_
19970527	70,000	_	1,900	_	_	-	_
19970612	21,000	_	620	_	_	-	_
19970707	4,000	_	580	_	120	10	16
19970804	13,000	_	460	_	<3	12	57
19970908	6,800	_	580	_	к28	_	_
19971208	8,000	_	320	_	_	_	_
19980112	1,500	_	98	_	_	_	_
19980209	1,600	_	240	_	_	_	_
19980309	13,000	_	520	_	_	_	_
19980406	1,100	_	^к зо	_	_	_	_
19980803	-	870	810	650	_	150	<1
				050		150	< <u>1</u>
ishtrap Creek at Fl 19970408		en, 12212100, site	3 280				
	5,500	-		-	_	_	_
19970506	33,000	_	4,000	_	_	-	_
19970529	77,000	_	5,900	-	-	-	-
19970610	7,000	-	230	-	22	0	6
19970709	190,000	-	5,200	-	77	7	4
19970806	6,700	-	3,200	-	<3	31	31
19970910	6,000	-	1,200	-	9	-	-
19971210	7,100	-	87	-	-	-	-
19980114	4,500	-	140	-	-	-	-
19980123	36,000	-	2,800	-	-	-	-
19980211	2,600	-	220	-	-	-	-
19980311	2,500	_	410	-	-	-	-
19980408	1,800	-	140	_	-	-	_
19980803	_	1,000	650	330	_	43	<1
ig Soos Creek abo	ve Hatchery near A	Auburn, 12112600	, site 8				
19970415	160	_	30	_	_	_	_
19970422	790	_	70	_	_	_	_
19970515	2,400	_	21	_	_	_	_
19970617	760	_	160	_	к5	76	8
19970715	2,000	_	^K 60	_	К4	8	37
19970812	2,000	_	140	_	к5	_	_
19970826	6,500	_	750	_	_	_	_
19970916	2,000	_	360	_	_	_	_
Jewaukum Creek n	ear Black Diamon	d 12108500 site	a a a a a a a a a a a a a a a a a a a				
19980804		210	190	150	_	58	2
Green River above	Twin Comp Croat						
19970424	<1 <1 <1 <1 <1	near Lester, 12103	<1 <1 <5380, site 10	_	_	_	_
19970521	24		<1	_	_	_	_
	24	—	~1	—	к1	_ _1	7
19970616 19970624	- 77	-	 K10	-		<1	17
		_		_	<3	43	
19970714	66 160	_	<1 K1	_	<1	3	21
10070011	(60)	_		_	_	_	_
19970811 19970915	180		<1				

Table 34. Pesticide and volatile organic compounds in storm samples collected on October 4, 1996, from Springbrook Creek, site 7, in the Puget Sound Basin study unit, Washington

[Values are in micrograms per liter unless otherwise noted. Number in parentheses below parameter or compound name is the U.S. Geological Survey's National Water Information System code. ft³/s, cubic feet per second; ^E, estimated; –, no data]

Time	Discharge, instantaneous (ft ³ /s) (00061)	2,6-Dieth aniline, diss (82660)	olved dia	etochlor, ssolved 49260)	Alachl dissolv (46342	ed dis	ha-HCH, solved 4253)	diss	azine, solved 1632)	Azinphos- methyl, dissolved (82686)	Benfluralin, dissolved (82673)
1530	76	< 0.00	3 <	< 0.002	< 0.00	2 <	0.002	<	:0.001	< 0.001	< 0.002
2010	89	<.00	13	<.002	<.00	2	<.002		<.001	<.001	<.002
Time	Butylate, dissolved (04028)	Carbaryl, dissolved (82680)	Carbofur dissolv (82674	ed	Chlorpyrifos, dissolved (38933)	Cyana disso (040	lved	<i>p,p</i> '-DI dissolv (34653	ed dissol	ved atrazine,	Diazinon, dissolved (39572)
1530	< 0.002	< 0.003	< 0.003	5	< 0.004	< 0.0	004	<0.006	5 <0.0	02 <0.002	0.032
2010	<.002	<.003	<.003	;	<.004	<.0	004	<.006	5 <.0	02 <.002	.037
Time	Dieldrin, dissolved (39381)	Disulfoton, dissolved (82677)	EPTC, dissolved (82668)	Ethalflura dissolve (82663)	ed diss	rophos, olved 672)	Fonof dissol (0409	ved	Lindane (<i>gamma</i> - HCH), dissolved (39341)	Linuron, dissolved (82666)	Malathion, dissolved (39532)
1530	< 0.001	< 0.017	< 0.002	< 0.004	<0.0	003	< 0.00	3	< 0.004	< 0.002	< 0.005
2010	<.001	<.017	<.002	<.004	<.(003	<.00	3	<.004	<.002	<.005
Time	Metolachlor, dissolved (39415)	Metribuzin, dissolved (82630)	Molinate, dissolved (82671)	Naprop amide, dissolve (82684)	dissc d (394	olved	Parathi methy dissolv (8266)	vl, ved	Pebulate, dissolved (82669)	Pendimethalin, dissolved (82683)	c <i>is</i> -Permethrin dissolved (82687)
1530	0.023	< 0.004	< 0.004	< 0.003	<0.	004	< 0.00	6	< 0.004	< 0.004	< 0.005
2010	.017	<.004	<.004	<.003	<.	004	<.00	6	<.004	<.004	<.005
Time	Phorate, dissolved (82664)	Prometon, dissolved (04037)	Propachlor, dissolved (04024)	Prop disso (826	lved dis	pargite, solved 82685)	diss	zamide, solved 2676)	Simazine dissolve (04035)	-	, Terbacil, dissolved (82665)
1530	< 0.002	^E 0.015	< 0.007	< 0.0	004 <0	0.013	<0.	.003	< 0.005	< 0.01	< 0.007
2010	<.002	.019	<.007	<.0	04 <	<.013	<.	.003	<.005	<.01	<.007
Time	Terbufos, dissolved (82675)	Thiobencarb, dissolved (82681)	Triallate, dissolved (82678)	dis	luralin, solved d 2661)	Silvex, lissolved (39762)	2,4,! disso (397	lved	2,4-D, dissolved (39732)	2,4-DB, dissolved (38746)	3-Hydroxy- carbofuran, dissolved (49308)
1530	< 0.013	< 0.002	< 0.001	<0.	002	< 0.02	<0.0)4	1.2	<0.24	< 0.01
2010	<.013	<.002	<.001	<.	002	<.02	<.()4	< 0.15	<.24	<.01
Time	4,6-Dinitro-2- methyl- phenol, dissolved (49299)	Acifluorfen, dissolved (49315)	Aldicarb, dissolved (49312)	Aldic sulfo dissol (4931	ne, sulf ved dis:	licarb foxide, solved 9314)	Bentaz dissol (3871	ved	Bromacil, dissolved (04029)	Bromoxynil, dissolved (49311)	Carbaryl, dissolved (49310)
	(45255)										
1530	<0.42	<0.04	<0.55	<0.1	0 <	0.02	< 0.0	1	< 0.04	<0.04	< 0.01

 Table 34.
 Pesticide and volatile organic compounds in storm samples collected on October 4, 1996, from Springbrook Creek, site 7, Puget Sound Basin study unit, Washington—Continued

Time	Carbofuran, dissolved (49309)	Chloramben, dissolved (49307)	Chlorothalonil dissolved (49306)	, Clopyralid dissolved (49305)		Dicamba, dissolved (38442)	Dichlo- benil, dissolved (49303)	Dichlorprop, dissolved (49302)	Dinoseb, dissolved (49301)
1530	<0.11	< 0.42	<0.48	< 0.23	< 0.02	< 0.04	<1.2	< 0.03	< 0.04
2010	<.11	<.42	<.48	<.23	<.02	<.04	<1.2	<.03	<.04
Time	Diuron, dissolved (49300)	Fenuron, dissolved (49297)	Fluometuron, dissolved (38811)	Linuron, dissolved (38478)	MCPA, dissolved (38482)	MCPB, dissolved (38487)	Methiocarb, dissolved (38501)	Methomyl dissolved (49296)	
1530	0.56	< 0.01	< 0.04	< 0.02	< 0.17	< 0.14	< 0.03	< 0.02	< 0.01
2010	^E 2.4	<.01	<.04	<.02	<.17	<.14	<.03	<.02	<.01
Time	Norflurazon, dissolved (49293)	Oryzalin, dissolved (49292)	Oxamyl, dissolved (38866)	Picloram, dissolved (49291)	Propham, dissolved (49236)	Propoxur, dissolved (38538)	Triclopyr, dissolved (49235)	Bromo- dichloro- methane, total (32101)	Tetrachloro- methane, total (32102)
1530	< 0.02	< 0.31	< 0.02	< 0.05	< 0.04	< 0.04	1.3	<0.2	<0.1
2010	<.02	<.31	<.02	<.05	<.04	<.04	<0.25	<.2	<.1
Time	1,2-Dichloro- ethane, total (32103)	Tribromo- methane, total (32104)	Dibromo- chloro- methane, total (32105)	Trichloro- methane, total (32106)	Methyl- benzene, total (34010)	Benzene, total (34030)	Acrolein, total (34210)	2-Propene- nitrile, total (34215)	Chloro- benzene, total (34301)
1530	< 0.1	< 0.4	<0.2	E0.01	< 0.1	< 0.1	<4	<4	< 0.1
2010	<.1	^E .03	<.2	^E .01	<.1	<.1	<4	<4	<.1
Time	Chloro- ethane, total (34311)	Ethylbenzene, total (34371)	1,1,1,2,2,2- Hexachloro- ethane, total (34396)	Bromo- methane, tota (34413)	Chloro- methane, total (34418)	Dichloro- methane, to (34423)	Tetra- chloro- tal ethene, total (34475)	Trichloro- fluoro- methane, total (34488)	1,1-Dichloro- ethane, total (34496)
1530	^E 0.1	< 0.1	<0.1	< 0.2	<0.4	<0.2	<0.1	< 0.2	<0.1
2010	^E .1	^E .01	<.1	<.2	<.4	<.2	_	<.2	<.1
Time	1,1- Dichloro- ethene, total (34501)	1,1,1-Trichloro- ethane, total (34506)	1,1,2-Trichlo ethane, tot (34511)	henzei	ne, propane, (3454)	total ether	oro- Trichloro ne, benzene I total		1,4-Dichloro- benzene, total (34571)
1530	< 0.2	< 0.1	<0.2	<0.	1 <0.1	<0	0.1 <0.4	< 0.1	< 0.1
2010	<.2	<.1	<.2	<.	1 <.1	<	<.1 <.4	<.1	<.1
Time	Dichloro- difluoro- methane, total (34668)	Naphthalene, total (34696)	trans-1,3- Dichloro-propene total (34699)	<i>cis</i> -1,3- , Dichloro- propene, tota (34704)	Chloro- l ethene, total (39175)	Trichloro- ethene, total (39180)	Hexachloro- butadiene, total (39702)	Bromo- ethene, total (50002)	ithyl <i>tert</i> -butyl ether, total (50004)
1530	<0.4	<0.4	<0.2	< 0.2	< 0.2	< 0.1	<0.4	<0.2	<0.2
2010	<.4	<.4	<.2	<.2	<.2		<.4	<.2	<.2

 Table 34.
 Pesticide and volatile organic compounds in storm samples collected on October 4, 1996, from Springbrook Creek, site 7, Puget Sound Basin study unit, Washington—Continued

Time	<i>tert</i> -Amyl methyl ether, total (50005)	<i>cis</i> -1,2-Dichloro- ethene, total (77093)	Ethenyl- benzene, total (77128)	1,2-Dimethyl- benzene, total (77135)	1,2,4- Trimethyl- benzene, total (77222)	(1-Methyl- ethyl)- benzene, total (77223)	<i>n</i> -Propyl- benzene, total (77224)	<i>n</i> -Butyl- benzene, total (77342)	1,2,3-Trichloro- propane, total (77443)
1530	<0.2	E0.01	<0.1	<0.1	<0.1	< 0.1	<0.1	<0.1	<0.4
2010	<.2	^E .01	<.1	<.1	<.1	<.1	<.1	<.1	<.4
Time	1,2,3-Trichloro- benzene, total (77613)	1,2-Dibromo- ethane, total (77651)	1,1,2- Trichloro- 1,2,2-trifluoro- ethane, total (77652)	Methyl <i>tert</i> - butyl ether, total (78032)	Diisopropyl ether, total (81577)	1,2- Dibromo-3- chloro- propane, total (82625)	benzene, total (77224) <i>n</i> -Butyi- benzene, total (77342) <0.1 <0.1 <.1 <.1 1,3 & 1,4- Dimethyl- benzene, total (85795) Dibromo- methane, total (30217) <0.1 <.1 <0.1 <.1 <1.3 & 1,4- Dimethyl- benzene, total (85795) Dibromo- methane, total (30217) <0.1 <0.2 <.1 <.2 2-Hexanone, (77103) 1,1- Dichloro- propene, total (77168) <10 <0.1 <10 <.1		1,1,2,2- Tetrachloro- ethane, total (34516)
1530	<0.4	<0.2	<0.1	< 0.2	< 0.2	<1	<0.1	< 0.2	<0.2
2010	<.4	<.2	<.1	<.2	<.2	<1	<.1	<.2	<.2
Time	Methyl acrylate, total (49991)	1,2,3,4- Tetramethyl- benzene, total (49999)	1,2,3,5- Tetramethyl- benzene, total (50000)	trans-1,4- Dichloro-2- butene, total (73547)	Ethyl meth- acrylate, total (73570)	Carbon disulfide, total (77041)		Dichloro- propene, total	2,2-Dichloro- propane, total (77170)
1530	<4	<0.1	<0.1	<10	<2	< 0.1	<10	< 0.1	<0.1
2010	<4	<.1	<.1	<10	<2	^E .01	<10	<.1	<.1
Time	1,3-Dichloro- propane, total (77173)	2-Ethyltoluene, total (77220)	1,2,3- Trimethyl- benzene, total (77221)	1,3,5- Trimethyl- benzene, tota (77226)	1-Chloro-2- methyl- I benzene, tota (77275)	1-Chloro-4- methyl- benzene, total (77277)	chloro- methane,	propyl)- benzene,	(1,1-Dimethyl- ethyl)-benzene, total (77353)
1530	<0.1	<0.1	<0.1	<0.1	<0.1	< 0.1	<0.2	<0.1	<0.1
2010	<.1	<.1	<.1	<.1	<.1	<.1	<.2	<.1	<.1
Time	1-lsopropyl-4- methyl-benzene, total (77356)	lodomethane, tota (77424)	1,1,1,2-Tetra- al chloro- ethane, total (77562)	3-Chloro-1- propene, total (78109)	4-Methyl-2- pentanone, tota (78133)	Acetone, al total (81552)	Bromo- benzene, total (81555)	Diethyl ′ether, total (81576)	Methyl acrylnitrile, total (81593)
1530	<0.1	<0.1	<0.1	<0.2	<10	E ₇	< 0.1	<0.2	<4
2010	<.1	<.1	<.1	<.2	<10	E ₇	<.1	<.2	<4
Time	2-Butanone, total (81595)	Methyl methacrylate, tota	Tetrahydro- al furan, total	_					

	(01333)	(81597)	(81607)
1530	E2	<2	<10
2010	<10	<2	<10

Table A1. Minimum reporting levels for major ions and trace metals
 analyzed in filtered surface-water samples by inductively coupled plasma, laboratory schedule 2701

[USGS NWIS code: U.S. Geological Survey National Water Information System No.; CAS No.: Chemical Abstracts Service No.; MRL, minimum reporting level; mg/L, milligrams per liter; μ g/L, micrograms per liter; °C, degrees Celsius; -, no value]

Compound	USGS NWIS code	CAS No.	MRL (mg/L, unless otherwise noted)
Calcium	00915	7440-70-2	0.02
Magnesium	00925	7439-95-4	.004
Sodium	00930	7440-23-5	.06
Potassium	00935	7440-09-7	.1
Iron, in µg/L	01046	7439-89-6	10
Manganese, in µg/L	01056	7439-96-5	3
Chloride	00940	16887-00-6	.1
Sulfate	00945	14808-79-8	.1
Fluoride	00950	16984-48-8	.1
Silica	00955	7631-86-9	.05
Residue on evaporation at 180 °C	70300	_	10

Table A2. Minimum reporting levels for nutrients analyzed in filtered and whole surface-water samples, laboratory schedule 2702

[USGS NWIS code: U.S. Geological Survey National Water Information System No.; CAS No.: Chemical Abstracts Service No.; MRL, minimum reporting level; LRL, laboratory reporting level; mg/L, milligrams per liter; N, nitrogen; P, phosphorus; –, no value]

Compound	USGS NWIS code	CAS No.	MRL/LRL (mg/L)
Nitrogen, ammonia, dissolved, as N	00608	7664-41-7	¹ 0.015, ² 0.02
Nitrogen, nitrite, dissolved, as N	00613	14797-65-0	.01
Nitrogen, ammonia + organic, dissolved, as N	00623	17778-88-0	¹ .2, ² .1
Nitrogen, ammonia + organic, total, as N	00625	17778-88-0	¹ .2, ² .1
Nitrogen, nitrite + nitrate, dissolved, as N	00631	_	.05
Phosphorus, total, as P	00665	7723-14-0	.01
Phosphorus, dissolved, as P	00666	7723-14-0	.01
Phosphorus, dissolved,	00671	14265-44-2	.01
orthophosphate, as P			

¹Prior to November 1997. ²After November 1997.

Table A3. Minimum reporting levels for organic carbon analyzed in surface-water samples, laboratory schedule 2075

[USGS NWIS code: U.S. Geological Survey National Water Information System No.; CAS No.: Chemical Abstracts Service No.; MRL, minimum reporting level; LRL, laboratory reporting level; mg/L, milligrams per liter; -, no value]

Compound	USGS NWIS code	CAS No.	MRL/LRL (mg/L)
Organic carbon, suspended	00689		¹ 0.1, ² 0.2
Organic carbon, dissolved	00681		.1

¹Prior to November 1997.

²After November 1997.

Table A4. Minimum reporting levels for pesticides and transformation products analyzed in filtered surface-water samples by gas chromatography/mass spectrometry, laboratory schedule 2010

Pesticide or degradation product	Туре	USGS NWIS code	CAS No.	MRL (μg/L)
2,6-Diethylaniline	Transformation product	82660	579-66-8	0.003
Acetochlor	Herbicide	49260	34256-82-1	.002
Alachlor	Herbicide	46342	15972-60-8	.002
Atrazine	Herbicide	39632	1912-24-9	.001
Azinphos-methyl	Insecticide	82686	86-50-0	.001
Benfluralin	Herbicide	82673	1861-40-1	.002
Butylate	Herbicide	04028	2008-41-5	.002
Carbaryl	Insecticide	82680	63-25-2	.003
Carbofuran	Insecticide	82674	1563-66-2	.003
Chlorpyrifos	Insecticide	38933	2921-88-2	.004
Cyanazine	Herbicide	04041	21725-46-2	.004
,p'-DDE	Transformation product	34653	72-55-9	.006
DCPA	Herbicide	82682	1861-32-1	.002
Deethylatrazine	Transformation product	04040	6190-65-4	.002
Diazinon	Insecticide	39572	333-41-5	.002
Dieldrin	Insecticide	39381	60-57-1	.001
Disulfoton	Insecticide	82677	298-04-4	.017
EPTC	Herbicide	82668	759-94-4	.002
Ethalfluralin	Herbicide	82663	55283-68-6	.004
Ethoprophos	Insecticide	82672	13194-48-4	.003
Fonofos	Insecticide	04095	944-22-9	.003
llpha-HCH	Insecticide ¹	34253	319-84-6	.002
Lindane (gamma-HCH)	Insecticide	39341	58-89-9	.004
Linuron	Herbicide	82666	330-55-2	.002
Malathion	Insecticide	39532	121-75-5	.005
Metolachlor	Herbicide	39415	51218-45-2	.002
Aetribuzin	Herbicide	82630	21087-64-9	.004
Molinate	Herbicide	82671	2212-67-1	.004
Napropamide	Herbicide	82684	15299-99-7	.003
Parathion	Insecticide	39542	56-38-2	.004
Parathion-methyl	Insecticide	82667	298-00-0	.006
Pebulate	Herbicide	82669	1114-71-2	.004
Pendimethalin	Herbicide	82683	40487-42-1	.004
eis-Permethrin	Insecticide	82687	54774-45-7	.005
Phorate	Insecticide	82664	298-02-2	.002
Prometon	Herbicide	04037	1610-18-0	.018
Propachlor	Herbicide	04024	1918-16-7	.007
Propanil	Herbicide	82679	709-98-8	.004
Propargite	Insecticide	82685	2312-35-8	.013
Propyzamide	Herbicide	82676	23950-58-5	.003
Simazine	Herbicide	04035	122-34-9	.005
Tebuthiuron	Herbicide	82670	34014-18-1	.010
Terbacil	Herbicide	82665	5902-51-2	.007
Terbufos	Insecticide	82675	13071-79-9	.013
Thiobencarb	Herbicide	82681	28249-77-6	.002
Friallate	Herbicide	82678	2303-17-5	.002
Frifluralin	Herbicide	82661	1582-09-8	.001
Surrogate recoveries	HEIDICIUE	02001	1302-07-0	MRL (percent)
Diazinon-d ₁₀ (surrogate)		91063	100155-47-3	0.1

[USGS NWIS code: U.S. Geological Survey National Water Information System No.; CAS No.: Chemical Abstracts Service No.; MRL, minimum reporting level; µg/L, micrograms per liter; DDE, dichlorodiphenyldichloroethylene; DCPA, dimethyltetrachloroterephthalate; EPTC, S-ethyl dipropylthiocarbamate; HCH, hexachlorocyclohexane; –, no value]

¹Pesticide can be a component of the technical mixture of lindane as well as a transformation product of lindane (Larson and others, 1997).

Table A5. Minimum reporting levels for pesticides and transformation products analyzed in filtered surface-water samples by high-performance liquid chromatography/photodiode-array detection, laboratory schedule 2051

[USGS NWIS code: U.S. Geological Survey National Water Information System No. CAS No.; Chemical Abstracts Service No.; MRL, minimum reporting level; µg/L, micrograms per liter; 2,4-5-T, (2,4-5-trichlorophenoxy) acetic acid; 2,4-DB, 4-(2,4-dichlorophenoxy) butyric acid; MCPA, (4-chloro-2-methylphenoxy) acetic acid; MCPB, 4-(4-chloro-o-tolyloxy)butyric acid; BDMC, 4-bromo-3,5-dimethyl phenyl-nmethylcarbamate; –, no value]

Pesticide or degradation product	Туре	USGS NWIS code	CAS No.	MRL (μg/L)
2,4,5-T	Herbicide	39742	93-76-5	0.035
2,4-D	Herbicide	39732	94-75-7	.15
2,4-DB	Herbicide	38746	94-82-6	.24
2-(2,4,5-Trichlorophenoxy) propionic acid	Herbicide	39762	93-72-1	.021
3-Hydroxycarbofuran	Transformation product	49308	16655-82-6	.014
4,6-Dinitro-2-methylphenol	Herbicide	49299	534-52-1	.42
Acifluorfen	Herbicide	49315	50594-66-6	.035
Aldicarb	Insecticide	49312	116-06-3	.55
Aldicarb sulfone	Transformation product	49313	1646-88-4	.10
Aldicarb sulfoxide	Transformation product	49314	1646-87-3	.021
Bentazon	Herbicide	38711	25057-89-0	.014
Bromacil	Herbicide	04029	314-40-9	.035
Bromoxynil	Herbicide	49311	1689-84-5	.035
Carbaryl	Insecticide	49310	63-25-2	.008
Carbofuran	Insecticide	49309	1563-66-2	.12
Chloramben	Herbicide	49307	133-90-4	.42
Chlorothalonil	Insecticide	49306	1897-45-6	.48
Clopyralid	Herbicide	49305	1702-17-6	.23
Dacthal monoacid	Degradation product	49304	887-54-7	.017
Dicamba	Herbicide	38442	1918-00-9	.035
Dichlobenil	Herbicide	49303	1194-65-6	1.2
Dichlorprop	Herbicide	49302	120-36-5	.032
Dinoseb	Herbicide	49301	88-85-7	.035
Diuron	Herbicide	49300	330-54-1	.020
Fenuron	Herbicide	49297	101-42-8	.013
Fluometuron	Herbicide	38811	2164-17-2	.035
Linuron	Herbicide	38478	330-55-2	.018
MCPA	Herbicide	38482	94-74-6	.17
MCPB	Herbicide	38487	94-81-5	.14
Methiocarb	Insecticide	38501	2032-65-7	.026
Methomyl	Insecticide	49296	16752-77-5	.017
Neburon	Herbicide	49294	555-37-3	.015
Norflurazon	Herbicide	49293	27314-13-2	.024
Oryzalin	Herbicide	49292	19044-88-3	.31
Oxamyl	Insecticide	38866	23135-22-0	.018
Picloram	Herbicide	49291	1918-02-1	.05
Propham	Herbicide	49236	122-42-9	.035
Propoxur	Insecticide	38538	114-26-1	.035
Triclopyr	Herbicide	49235	55335-06-3	.25
Surrogate recoveries				MRL (percent)
BDMC (surrogate)		99835	-	.1

 Table A6.
 Minimum reporting levels for volatile organic compounds analyzed in whole surface-water samples by purge and trap chromatography/mass

 spectrometry, laboratory schedule 2020

[USGS NWIS code, U.S. Geological Survey National Water Information System No.; CAS No., Chemical Abstracts Service No.; LRL, 1999 laboratory reporting level; MRL, laboratory minimum reporting level; µg/L, micrograms per liter; –, no value]

Compound (Common name)	USGS NWIS code	CAS No.	LRL Compound (µg/L)		USGS NWIS code	CAS No.	LRL (µg/L)
1,1,1,2-Tetrachloroethane	77562	630-20-6	0.044	Benzene	34030	71-43-2	0.1
1,1,1-Trichloroethane	34506	71-55-6	.032	Bromobenzene	81555	108-86-1	.036
1,1,2,2-Tetrachloroethane	34516	79-34-5	.13	Bromochloromethane	77297	74-97-5	.044
1,1,2-Trichloroethane	34511	79-00-5	.064	Bromodichloromethane	32101	75-27-4	.048
1,1,2-Trichloro-1,2,2- trifluoroethane (Freon 113)	77652	76-13-1	.032	Bromoethene	50002	593-60-2	.1
1,1-Dichloroethane	34496	75-34-3	.066	Tribromomethane (Bromoform)	32104	75-25-2	.1
1,1-Dichloroethene	34501	75-35-4	.044	Bromomethane (Methyl bromide)	34413	74-83-9	.15
1,1-Dichloropropene	77168	563-58-6	.026	<i>n</i> -Butylbenzene	77342	104-51-8	.19
1,2,3,4-Tetramethylbenzene (Prehnitene)	49999	488-23-3	.23	Carbon disulfide	77041	75-15-0	.37
1,2,3,5-Tetramethylbenzene (Isodurene)	50000	527-53-7	.2	Chlorobenzene	34301	108-90-7	.028
1,2,3-Trichlorobenzene	77613	87-61-6	.27	Chloroethane	34311	75-00-3	.12
1,2,3-Trichloropropane	77443	96-18-4	.16	Trichloromethane (Chloroform)	32106	67-66-3	.052
1,2,3-Trimethylbenzene	77221	526-73-8	.12	Chloromethane (Methyl chloride)	34418	74-87-3	.25
1,2,4-Trichlorobenzene	34551	120-82-1	.19	Dibromochloromethane	32105	124-48-1	.18
1,2,4-Trimethylbenzene	77222	95-63-6	.056	Dibromomethane	30217	74-95-3	.05
1,2-Dibromo-3-chloropropane	82625	96-12-8	.21	Dichlorodifluoromethane	34668	75-71-8	.14
1,2-Dibromoethane	77651	106-93-4	.036	Dichloromethane (Methylene chloride)	34423	75-09-2	.38
1,2-Dichlorobenzene	34536	95-50-1	.048	Diethyl ether (Ethyl ether)	81576	60-29-7	.17
1,2-Dichloroethane	32103	107-06-2	.13	Diisopropyl ether	81577	108-20-3	.098
1,2-Dichloropropane	34541	78-87-5	.068	Ethyl methacrylate	73570	97-63-2	.28
1,3,5-Trimethylbenzene	77226	108-67-8	.044	Ethyl <i>tert</i> -butyl ether	50004	637-92-3	.054
1,3-Dichlorobenzene	34566	541-73-1	.054	Ethylbenzene	34371	100-41-4	.03
1,3-Dichloropropane	77173	142-28-9	.12	Hexachlorobutadiene	39702	87-68-3	.14
1,4-Dichlorobenzene	34571	106-46-7	.05	1,1,1,2,2,2-Hexachloroethane (Hexachloroethane)	34396	67-72-1	.36
2,2-Dichloropropane	77170	594-20-7	.078	(1-Methylethyl)benzene (Isopropylbenzene)	77223	98-82-8	.032
2-Butanone (Methyl ethyl ketone)	81595	78-93-3	1.6	Methyl acrylate	49991	96-33-3	1.4
1-Chloro-2-methylbenzene (o-Chlorotoluene)	77275	95-49-8	.042	Methyl acrylonitrile	81593	126-98-7	.57
2-Hexanone	77103	591-78-6	.7	Iodomethane (Methyl iodide)	77424	74-88-4	.21
3-Chloro-1-propene	78109	107-05-1	.2	Methyl methacrylate	81597	80-62-6	.35
1-Chloro-4-methylbenzene (p-Chlorotoluene)	77277	106-43-4	.056	Naphthalene	34696	91-20-3	.25
1-Isopropyl-4-methylbenzene (p-Isopropyltoluene)	77356	99-87-6	.11	Ethenylbenzene (Styrene)	77128	100-42-5	.042
4-Methyl-2-pentanone (Methyl isobutyl ketone)	78133	108-10-1	0.37	Tetrachloroethene	34475	127-18-4	0.1
Acetone	81552	67-64-1	5	Tetrachloromethane	32102	56-23-5	.088
2-Propenenitrile (Acrylonitrile)	34215	107-13-1	1.2	Tetrahydrofuran	81607	109-99-9	9.0

Table A6. Minimum reporting levels for volatile organic compounds analyzed in whole surface-water samples by purge and trap chromatography/mass spectrometry, laboratory schedule 2020—*Continued*

Compound (Common name)	USGS NWIS code	CAS No.	LRL (μ g/L)	Compound	USGS NWIS code	CAS No.	LRL (µg/L)
Methylbenzene (Toluene)	34010	108-88-3	0.05	Methyl <i>tert</i> -butyl ether (MTBE)	78032	1634-04-4	0.17
Trichloroethene	39180	79-01-6	.038	(1,1-Dimethylethyl)benzene	77353	98-06-6	.1
Trichlorofluoromethane	34488	75-69-4	.09	tert-Amyl methyl ether	50005	994-05-8	.11
Chloroethene (Vinyl chloride)	39175	75-01-4	.11	trans-1,2-Dichloroethene	34546	156-60-5	.032
cis-1,2-Dichloroethene	77093	156-59-2	.038	trans-1,3-Dichloropropene	34699	10061-02-6	.13
cis-1,3-Dichloropropene	34704	10061-01-5	.09	trans-1,4-Dichloro-2-butene	73547	110-57-6	.7
1,3-plus-1,4-Dimethylbenzene (<i>m</i> , <i>p</i> -Xylene)	85795		.06				
<i>n</i> -Propylbenzene	77224	103-65-1	.042	Surrogate recoveries			MRL
2-Ethyltoluene (o-Ethyltoluene)	77220	611-14-3	.1	1,2-Dichloroethane-d4 (surrogate)	99832	17060-07-0	.1
1,2-Dimethylbenzene (o-Xylene)	77135	95-47-6	.06	1,4-Bromofluorobenzene (surrogate)	99834	460-00-4	.1
(1-Methylpropyl)benzene	77350	135-98-8	.048	Toluene-d8 (surrogate)	99833	2037-26-5	.1

APPENDIX B. QUALITY ASSURANCE/QUALITY CONTROL— METHODS, RESULTS, AND DISCUSSION

Between December 1995 and February 1998, 32 blank-water samples, prepared with inorganic-grade water, were submitted for major ion analyses. A total of six compounds, mostly all cations, were detected in these samples (table B1). Silica was the most frequently detected compound, found in 12 of the 32 blank-water samples; the presence of silica was likely an artifact of the glass ampoules for the acid preservative. Concentrations of all the detected compounds were low and, except for compounds in two blank-water samples, well below the minimum concentrations detected in streamwater from the site where the blank was prepared. One blank prepared at the lower Nooksack (site 3) had a chloride concentration of 0.17 mg/L (milligrams per liter) and a minimum environmental sample concentration of 0.44 mg/L, and one blank at the upper Green (site 10) had an iron concentration of 3.7 µg/L (micrograms per liter) and an environmental sample concentration reported at less than $3 \mu g/L$ on the day of preparation. Thus, field or laboratory contamination of samples for major ions analyses was generally not of concern and no adjustments were made to the database.

Five compounds were detected in 34 blank-water samples prepared for nutrient analyses between December 1995 and February 1998 (table B2). There were no detections of organic nitrogen (total or dissolved) or of dissolved phosphorus. In these blanks, nitrate was detected most frequently, in 11 of the 34 blank-water samples; orthophosphate phosphorus was detected next most frequently, in 5 of the 34 samples. For nitrate, concentrations in the blanks were considerably lower, generally from four times to an order of magnitude lower, than in the environmental samples at the site where the blanks were prepared. At the North Fork Skokomish (site 2) and the upper Nooksack (site 5), where water was naturally low in nutrients, the concentration of orthophosphate in one blank sample per site was equal to or larger than the environmental concentration on the day of collection. This was true also for concentrations of nitrite, nitrate, and ammonia in one blank sample prepared at the upper Green. These few occurrences indicated that systematic bias was not a problem. Because all sample collection and processing equipment was rinsed with native water before samples were collected and split into subsamples, it is believed that the data sets for these sites are of satisfactory quality. Therefore, no values were deleted from the database, but for reference, the value of the environmental sample on the day of blank preparation is listed in parentheses alongside the value of the blank in table B2.

Between December 1995 and February 1998, 30 blank-water samples were prepared for organic carbon analyses. Dissolved organic carbon was detected in 27 of these samples and suspended organic carbon in 15 (table B3). Some of the carbon in the blanks was from the source water; in half of the source-water samples, levels of dissolved organic carbon ranged from 0.1 to 0.7 mg/L. This level of carbon indicates some positive bias in a few samples from the Skokomish (site 1), North Fork Skokomish (site 2), Nooksack (sites 3 and 5), and upper Green (site 10), with environmental concentrations below the 10th percentile. These levels were unimportant for the range of concentrations found in samples from the other seven sites. The database was not adjusted or corrected for organic carbon found in the blank samples.

Sixteen blank-water samples for volatile organic compounds (VOCs) were prepared with non-nitrogengas-purged volatile-grade (VG) water and submitted between April 1996 and February 1997. A total of 18 compounds was detected in these blanks (<u>table B4</u>). One of the 18, bromodichloromethane, was not detected in any environmental samples so is not of concern. Of the remaining 17 compounds, 8 (trichloromethane, acetone, tetrahydrofuran, chlorobenzene, 2-butanone, ethenylbenzene (styrene), ethylbenzene, and benzene) were most likely present in the VG water.

Five compounds (1,3-plus-1,4-dimethylbenzene, 4-methyl-2-pentanone, acetone, chloromethane, and methylbenzene) were detected in nitrogen-gas-purged blanks but were not detected in the N2-purged VG water. The concentrations of these compounds (except for methylbenzene) were below the LRLs and are estimated. A compound detected in a blank sample was also detected in an environmental sample only four times: once each for carbon disulfide, chloromethane, 1,3-plus-1,4-dimethylbenzene, and 1,2dichloropropane. However, the concentrations in the environmental samples were equal to or greater than the highest concentration found in the corresponding blanks, indicating that the detection in the environmental sample was not caused by carryover of any contamination from the blank water. This indicates that the VOCs either were in the VG water or were introduced in an isolated event, and not the result of systematic contamination caused by the sampling equipment or procedures.

In the six blanks that were collected with the N₂purged VG water in December 1997 and May 1998, methylbenzene was detected four times, 1,3-plus-1,4dimethylbenzene three times, and acetone, benzene, chloromethane, and 4-methyl-2-pentanone once each (table B4). Of these compounds, the detection of benzene can be explained as its presence in the VG source water. The remaining compounds fell below the LRLs and the estimated concentrations were generally at or below the lower range of environmental detections. The general absence of VOCs in the N₂purged blanks indicates that the sampling equipment and procedures most likely did not introduce any systematic contamination into the environmental samples.

Methylbenzene was detected in 69 percent of non-N₂-purged blanks and in 66 percent of the N₂ - purged blanks, making it the most frequently detected compound in the blank samples. In most of the detections, methylbenzene concentrations were estimated to be below the LRLs. However, methylbenzene had the highest concentration of any compound detected in the blanks and was occasionally detected at concentrations above the LRL. Because the highest methylbenzene concentrations (greater than $0.5 \ \mu g/L$) were detected in both the blank and environmental samples, were clustered between September and October 1996, and were found at all four intensive fixed sites, the cause was believed to be contamination. Therefore, the eight environmental

methylbenzene detections during that time period that exceeded a concentration of 0.5 μ g/L were censored from the data set and are not included in any statistical or graphical presentation of data. Those detections have been censored with a V-code in the NWIS database, indicating that the concentrations are believed to be due to contamination.

Variability in sampling and analytical methods was measured with 26 pairs of split replicate samples for major ions, 29 pairs for nutrients, and 5 pairs for pesticides; and with 20 pairs of concurrent replicate samples for dissolved organic carbon and one pair of concurrent replicate samples for VOCs. The variability in each pair of samples was expressed as the relative percent difference in the concentrations. For all classes of compounds, occasionally one member of the pair would be reported as less than the MRL or LRL and the other member would be reported at a detectable concentration typically equal to the MRL or LRL, and percent differences for these pairs were not calculated. Most of the cations and anions concentrations had relative percent differences less than 10 percent (table B5) and the median differences for all the major ions were 6 percent or less. Variability between results was lowest for sulfate, which ranged from 0 to 5.4 percent, and highest for iron, which ranged from 0 to 58 percent. Variability tended to be larger for the nutrient analyses than for the major ions, ranging from 0 to 67 percent (table B6). The greatest percent differences typically occurred for pairs of samples with low concentrations near the analytical reporting limits, indicating that the inherent variability in these lowconcentration data needs to be considered in subsequent applications, such as load calculations and other analyses. Relative percent differences between pairs of organic carbon ranged from 0 to 40 percent for dissolved, and from 0 to 100 percent for suspended (table B7). As with nutrients, large percent differences were generally between replicate pairs with low concentrations. For the pesticides, differences ranged from 0 to 40 percent (table B8). The replicate VOC samples had detections of trichloromethane, methylbenzene, chloromethane, 1-isopropyl-4methylbenzene, and 4-methyl-2-pentanone. The concentrations for the replicates were identical for each of the detected compounds with the exception of methylbenzene, which had a difference of 0.01 μ g/L between the replicates. No changes were made to any of the inorganic or organic chemical data sets based on these replicate data.

For five pairs of field-matrix spiked water samples, recoveries for pesticide compounds ranged from about 10 to more than 300 percent, with generally lower recoveries for laboratory schedule 2051 compounds than for schedule 2010 compounds (fig. B1). For the majority of schedule 2010 analytes, recoveries were good and fairly precise ranging from about 60 to 140 percent. Those compounds with recoveries greatly different from this range included atrazine, azinphos-methyl, carbaryl, carbofuran, deethylatrazine, disulfoton, ethalfluralin, linuron, methyl-parathion, terbacil, and *cis*-permethrin. Low percent recoveries for some compounds, such as carbaryl, carbofuran, terbacil, and permethrin, indicated possible matrix interference for some samples collected at Thornton Creek. Conversely, high percent recoveries for compounds such as atrazine, azinphos-methyl, carbaryl, and carbofuran indicated possible positive bias for some samples collected at Thornton Creek, Fishtrap Creek, and the lower Nooksack River. For most schedule 2051 analytes, recoveries ranged from 20 to 50 percent (fig. B1). Generally low recoveries and precision for schedule 2051 have previously been reported (Wagner and Roberts, 1998; Anderson and others, 1996). For samples collected during this study, recoveries were particularly low for acifluorfen, aldicarb, aldicarb sulfone, chlorothalonil, clopyralid, and dichlobenil. Of these, only dichlobenil was detected in samples from the sites. Because of low recoveries and the large range in recoveries for the schedule 2051 analytes, there is potential in environmental water samples for falsenegative analytical results (Wagner and Roberts, 1998) and for the magnitude of a pesticide's concentration to be unknown (Anderson and others, 1996).

For eight pairs of field-matrix spiked samples for VOCs, recoveries and precision for VOCs in fieldspiked samples were good, ranging from mean recoveries of 71 to 101 percent and standard deviations from 3 to 26 percent (table B9). Compounds with the lowest mean recovery included bromoform and chloroethene (71 percent), and 1,4-dichlorobenzene (76 percent). Of these, both bromoform and 1,4-dichlorobenzene were detected in environmental water samples, but only bromoform was detected above the LRL. On the basis of the pesticide- and VOC-analyte recoveries determined on field-matrix spiked replicate samples, no changes or adjustments were made to the data sets.

All pesticide samples were spiked in the field with mixtures of surrogate analytes to monitor the precision and accuracy of analytical procedures. Mean recoveries for diazinon-d10 and alpha-HCH-d6 in samples from the four stations ranged from 99 to 108 percent (table B10). Mean recoveries of terbuthylazine tended to be a little higher than diazinon-d10 and alpha-HCH-d6 recoveries, ranging from 110 to 120 percent, and mean recoveries for BDMC for laboratory schedule 2051 tended to be a little lower, ranging from 88 to 92 percent. Surrogates for VOC analyses are not added in the field, but are added in the laboratory. Recoveries of the VOC surrogate analytes were also good, with mean recovery of 92 percent for 1,-2-dichloroethane-d4, 106 percent for toluene-d8, and 113 percent for 1,4bromofluorobenzene (table B11).

Table B1. Concentrations of major ions in field-blank water samples for the Puget Sound Basin study unit, Washington

				Compoun	d (USGS NV	VIS code), in	milligrams	per liter and d	issolved un	ess otherwi	se noted	
Station No.	Site No.	Sample date	Calcium (00915)	Silica (00955)	lron (01046) (μg/L)	Chloride (00940)	Magne- sium (00925)	Fluoride (00950)	Sodium (00930)	Manga- nese (01056) (µg/L)	Potas- sium (00935)	Sulfate (00945)
12061500	1	08-14-97	< 0.02	< 0.01	<3	< 0.1	< 0.01	< 0.1	< 0.2	<1	< 0.1	< 0.1
12061500	1	09-17-97	<.02	<.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12056500	2	05-28-96	.58	.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12056500	2	09 17-97	<.02	<.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12056500	2	11-13-97	<.02	<.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12213140	3	01-08-97	<.02	.04	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12213140	3	06-09-97	<.02	<.01	<3	.17	<.01	<.1	<.2	<1	<.1	<.1
12212100	4	04-24-96	.67	.01	6	<.1	<.01	<.1	<.2	<1	<.1	<.1
12212100	4	10-09-96	<.02	.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12212100	4	06-10-97	.02	<.01	<3	.16	<.01	<.1	<.2	<1	.1	<.1
12210700	5	12-02-95	<.02	.12	<3	.3	<.01	<.1	<.2	<1	<.1	<.1
12210700	5	04-08-97	<.02	<.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12210700	5	05-06-97	<.02	.03	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12210700	5	02-10-98	<.02	<.1	<1	<.1	<.004	<.1	<.1	<4	<.1	<.1
12113390	6	01-03-97	<.02	<.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12113390	6	06-18-97	.02	<.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12113390	6	11-14-97	<.02	.02	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12113375	7	12-12-95	<.02	.07	3	.1	<.01	<.1	<.2	<1	<.1	<.1
12113375	7	06-18-97	<.02	<.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12113375	7	11-14-97	<.02	.02	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12112600	8	07-15-97	.02	<.01	<3	<.1	.02	<.1	<.2	<1	<.1	<.1
12112600	8	09 16-97	<.02	<.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12112600	8	11-12-97	<.02	<.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12108500	9	05-15-97	<.02	.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12108500	9	12-15-97	<.02	<.1	<1	<.1	<.004	<.1	<.1	<4	<.1	<.1
12103380	10	05-21-97	<.02	<.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12103380	10	08-11-97	<.02	.02	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12103380	10	09 15-97	<.02	<.01	3.7	<.1	<.01	<.1	<.2	<1	<.1	<.1
12103380	10	11-06-97	<.02	<.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12128000	11	10-08-96	<.02	.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12128000	11	06-12-97	<.02	<.01	<3	<.1	<.01	<.1	<.2	<1	<.1	<.1
12128000	11	02-09-98	<.02	<.1	<1	<.1	<.004	<.1	<.1	<4	<.1	<.1

[USGS NWIS, U.S. Geological Survey National Water Information System; <, less than; µg, micrograms per liter]

Table B2. Concentrations of nutrients in field-blank water samples for the Puget Sound Basin study unit, Washington

[Values in parentheses are for environmental samples collected from the same site on the same date. USGS NWIS, U.S. Geological Survey National Water Information System; N, nitrogen; <, less than; -, missing value]

					Compound (L	JSGS NWIS cod	e), in milligrams	per liter		
Station No.	Site No	Sample date	Phosphorus, total (00665)	Dissolved phosphorus (00666)	Dissolved ortho- phosphate phosphorus (00671)	Dissolved nitrite, as N (00613)	Dissolved nitrite-plus- nitrate, as N (00631)	Dissolved ammonia, as N (00608)	Ammonia- plus- organic, as N, total (00625)	Dissolved ammonia- plus- organic, as N (00623)
12061500	1	08-14-97	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05	< 0.015	<0.2	<0.2
12061500	1	09-17-97	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12056500	2	05-28-96	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12056500	2	09-17-97	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12056500	2	11-13-97	<.01	<.01	.02 (.02)	<.01	<.05	<.02	<.1	<.1
12213140	3	06-09-97	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12212100	4	04-24-96	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12212100	4	10-09-96	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12212100	4	06-10-97	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12212100	4	07-08-97	<.01	<.01	.01 (.03)	<.01	<.05	<.015	<.2	<.2
12210700	5	12-02-95	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12210700	5	04-08-97	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12210700	5	05-06-97	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12210700	5	02-10-98	<.01	<.01	.02 (.01)	<.01	.06 (.22)	<.02	<.1	<.1
12113390	6	01-03-97	<.01	<.01	<.01	<.01	.05 (.45)	<.015	<.2	<.2
12113390	6	06-18-97	<.01	<.01	<.01	<.01	.06 (.22)	<.015	<.2	<.2
12113390	6	11-14-97	<.01	<.01	<.01	<.01	<.05	<.02	<.1	<.1
12113375	7	12-12-95	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12113375	7	06-18-97	<.01	<.01	<.01	<.01	.06 (.31)	<.015	<.2	<.2
12113375	7	11-14-97	<.01	<.01	<.01	<.01	<.05	<.02	<.1	<.1
12112600	8	07-15-97	<.01	<.01	<.01	<.01	.06 (.48)	<.015	<.2	<.2
12112600	8	09-16-97	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12112600	8	11-12-97	<.01	<.01	.01 (.03)	.02 (.03)	.07 (.84)		<.1	<.1
12108500	9	05-15-97	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12108500	9	12-15-97	.02 (.07)	<.01	<.01	.03 (.03)	.06 (2.32)	<.02	<.1	<.1
12103380	10	05-21-97	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12103380	10	08-11-97	<.01	<.01	<.01	<.01	.07 (.05)	.03 (.02)	<.2	<.2
12103380	10	09-15-97	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12103380	10	11-06-97	<.01	<.01	<.01	.01 (.01)	.07 (.07)	.06 (.061)	<.1	<.1
12128000	11	04-11-96	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12128000	11	10-08-96	.01 (.04)	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12128000	11	06-12-97	<.01	<.01	<.01	<.01	.09 (.98)	<.015	<.2	<.2
12128000	11	07-07-97	<.01	<.01	<.01	<.01	<.05	<.015	<.2	<.2
12128000	11	02-09-98	<.01	<.01	.02 (.04)	<.01	.06 (1.37)	<.02	<.1	<.1

 Table B3.
 Concentrations of dissolved and suspended organic carbon in field-blank water samples for the Puget Sound Basin study unit, Washington

[Values are in milligrams per liter. USGS NWIS, U.S. Geological Survey National Water Information System; <, less than; na, not analyzed]]

	6:44		Blank tune		pound WIS code)		Site	Comple	Blank time		pound WIS code)
Station No.	Site No.	Sample date	Blank type (99102)	Carbon, dissolved (00681)	Carbon, suspended (00689)	Station No.	No.	Sample date	Blank type (99102)	Carbon, dissolved (00681)	Carbon, suspended (00689)
12061500	1	04-11-97	source water	< 0.1	na	12056500	2	02-12-98	field	0.2	<.2
12061500	1	05-08-97	source water	<.1	na	12213140	3	08-07-96	field	.3	<.1
12056500	2	08-14-97	source water	<.1	na	12213140	3	08-07-96	field	.3	<.1
12056500	2	02-12-98	source water	<.1	na	12213140	3	08-07-96	field	.3	<.1
12213140	3	08-07-96	source water	.2	na	12213140	3	02-14-97	field	.9	.1
12213140	3	08-07-96	source water	.2	na	12212100	4	04-24-96	field	.6	.2
12213140	3	08-07-96	source water	<.1	na	12212100	4	07-09-96	field	.3	.1
12213140	3	02-14-97	source water	.7	0.2	12212100	4	01-07-97	field	.3	.3
12212100	4	01-07-97	source water	<.1	na	12212100	4	12-10-97	field	.2	<.2
12212100	4	12-10-97	source water	<.1	na	12210700	5	12-02-95	field	.3	.1
12210700	5	06-09-97	source water	<.1	na	12210700	5	06-09-97	field	<.1	.1
12210700	5	11-04-97	source water	.3	na	12210700	5	11-04-97	field	.2	<.2
12113390	6	02-06-97	source water	.1	na	12113390	6	09-12-96	field	.4	<.1
12113390	6	03-17-97	source water	.1	na	12113390	6	02-06-97	field	<.1	<.1
12113390	6	02-17-98	source water	<.1	na	12113390	6	03-17-97	field	.2	.1
12113375	7	03-17-97	source water	<.1	na	12113390	6	02-17-98	field	.1	<.2
12112600	8	04-15-97	source water	.2	na	12113375	7	12-12-95	field	.6	.3
12108500	9	04-15-97	source water	.1	na	12113375	7	03-17-97	field	0.7	0.6
12103380	10	06-16-97	source water	<.1	na	12112600	8	04-15-97	field	.2	.1
12128000	11	01-14-97	source water	.1	na	12112600	8	02-19-98	field	.1	<.2
12128000	11	01-12-98	source water	.1	na	12108500	9	04-15-97	field	.9	.1
12061500	1	04-11-97	field	.8	<.1	12103380	10	06-16-97	field	<.1	.1
12061500	1	05-08-97	field	.2	<.1	12128000	11	06-07-96	field	.4	.2
12061500	1	11-13-97	field	.7	<.2	12128000	11	01-14-97	field	.3	.1
12056500	2	05-28-96	field	.1	.1	12128000	11	01-12-98	field	.2	<.2
12056500	2	08-14-97	field	.2	na						

Table B4.Summary of volatile organic compounds detected in source, canister, and field blank-water samples for the Puget Sound Basin study unit,
Washington

VQL, National water of				

	NWQL lot analysis of non- N ₂ -purged VGW		llected with non- ged VGW	NWQL lot analysis of N ₂ -purged VGW		s collected with rged VGW	Environmental samples
Compound	Detected concentrations (µg/L)	Percentage of detections (number of detects)	Range of detected concentrations	Detected concentrations (µg/L)	Percentage of detections (number of detects)	Range of detected concentrations	Range of detected concentrations
1,2,4-Trimethylbenzene	ND	18.8 (3)	E0.007-E0.02	ND	ND	ND	E0.005-0.12
1,2-Dichloropropane	ND	31.3 (5)	E.01-E.02	ND	ND	ND	^E .01- ^E .03
1,2-Dimethylbenzene	ND	12.5 (2)	E.01-E.02	ND	ND	ND	^E .0071
1,3-plus-1,4- Dimethylbenzene	ND	37.5 (6)	^E .01- ^E .04	ND	50 (3)	^E 0.0061- ^E 0.0083	^E .0082
1,4-Dichlorobenzene	ND	37.5 (6)	^E .009- ^E .01	ND	ND	ND	E.002-E.01
2-Butanone	0.52, 1.1	37.5 (6)	^E .3- ^E .4	^E 0.01, ND	ND	ND	^E .1- ^E 1.4
1-Isopropyl-4- methylbenzene	ND	12.5 (2)	^E .005	ND	ND	ND	E.003-E.044
4-Methyl-2-pentanone	ND	ND	ND	ND	16.6 (1)	^E .28	^E .1- ^E 1.0
Acetone	1.4, 3.5	56.3 (9)	1.0-2.4	ND	16.6 (1)	^E .99	E1.0-12.5
Benzene	.02, .016	6.3 (1)	^E .04	ND, ^E .01	16.6 (1)	^E .012	^E .0091- ^E .1
Bromodichloromethane	ND	25 (4)	^E .01	ND	ND	ND	ND
Carbon disulfide	ND	18.8 (3)	E.003-E.01	ND	ND	ND	^E .007105
Chlorobenzene	ND, ^E .03	37.5 (6)	^E .004- ^E .01	ND	ND	ND	E.002-E.03
Chloromethane	ND	12.5 (2)	^E .04	ND	16.6 (1)	^E .0036	E.0085135
Ethenylbenzene	ND, ^E .015	31.3 (5)	^E .003- ^E .006	ND	ND	ND	^E .001- ^E .01
Ethylbenzene	ND, .037	25 (4)	^E .006- ^E .01	ND	ND	ND	E.002-E.06
Methylbenzene	ND, .031	68.8 (11)	^E .08-1.6	ND	66 (4)	^E .019- ^E .034	E.03-2.2
Tetrahydrofuran	ND, 2.4	50 (8)	^E .2- ^E .5	ND	ND	ND	^E .3
Trichloromethane	.04, ^E .039	87.5 (14)	^E .03- ^E .09	ND	ND	ND	^E .00516

Table B5. Concentrations of major ions in replicate environmental water samples for the Puget Sound Basin study unit, Washington

[Replicate types: 10-concurrent, 20-sequential, 30-split, 40-split-concurrent; compound detection values are in milligrams per liter except for iron and manganese, which are in micrograms per liter; USGS NWIS, U.S. Geological Survey National Water Information System; <, less than; --, not analyzed; nc, not calculated; relative percentage of difference = $\frac{|R1 - R2|}{|R1 - R2|} \times 100$, where R1 = sample 1 result and R2 = sample 2 result]

$$\left(\frac{R1+R2}{2}\right)$$

			Deal				Com	pound (USG	iS NWIS cod	le)			
Station No.	Sample date	Site No.	Repli- cate type	Calcium (00915)	Silica (00955)	lron (01046)	Chloride (00940)	Magne- sium (00925)	Fluoride (00950)	Sodium (00930)	Manga- nese (01056)	Potas- sium (00935)	Sulfate (00945)
12061500	01-07-98	1	30	6.39	10.864	<10	1.473	1.479	< 0.1	1.852	<4	0.1	0.95
			30	6.439	11.65	<10	1.531	1.536	<.1	1.86	<4	<.1	.98
Rela	tive percent	age of c	lifference	0.8	7	nc	3.9	3.8	nc	<1	nc	nc	3.1
12056500	09-17-97	2	30	7.087	3.606	11.3	0.485	0.538	<.1	0.927	<1	.13	2.357
			30	6.692	3.624	9.791	.436	.52	<.1	1.12	<1	.13	2.36
Rela	tive percent	age of c	lifference	5.7	<1	14	11	3.4	nc	19	nc	0	<1
12056500	01-07-98	2	30	12.364	5.527	<10	.917	.952	<.1	1.548	<4	.18	5.091
			30	12.465	5.592	<10	.921	.96	<.1	1.554	<4	.12	4.953
Rela	tive percent	age of c	lifference	<1	1.2	nc	<1	<1	nc	<1	nc	40	2.7
12213140	02-14-97	3	30	12	9.6	87	4	4	<.1	4.1	21	1.3	12
			30	13	10	89	4.1	4.1	<.1	4.3	22	1.3	12
Rela	tive percent	age of c	lifference	8	4.1	2.3	2.5	2.5	nc	4.8	4.7	0	0
12213140	11-04-97	3	30	7.798	6.818	64.193	1.707	2.336	<.1	1.892	5.715	.73	5.716
			30	7.857	6.852	57.389	1.776	2.338	<.1	1.909	5.503	.74	5.74
Rela	tive percent	age of c	lifference	<1	<1	11	4	<1	nc	<1	3.8	1.4	<1
12212100	07-09-96	4	30	29	18	390	11	7.7	<.1	9.3	92	2.3	37
			30	28	17	360	11	7.6	<.1	9.1	91	2.3	37
Rela	tive percent	age of c	lifference	3.5	5.7	8	0	1.3	nc	2.2	1.1	0	0
12212100	04-08-97	4	30	25.212	13.92	148.17	10.711	7.017	<.1	8.237	159.44	2.91	35.056
			30	25.108	13.804	118.93	10.728	6.971	<.1	8.212	159.44	2.97	34.971
Rela	tive percent	age of c	lifference	<1	<1	22	<1	<1	nc	<1	0	2	<1
12212100	02-11-98	4	30	24.53	16.734	165.39	9.631	6.562	<.1	8.333	161.68	2.8	30.692
			30	23.953	16.1	165.06	10.095	6.822	<.1	8.201	166.16	2.82	30.769
Rela	tive percent	age of c	lifference	2.4	3.9	<1	4.7	3.9	nc	1.6	2.7	<1	<1
12210700	03-11-97	5	30	10	8.3	21	1.1	3.1	<.1	1.7	6	.4	6.6
			30	11	8.8	25	1.1	3.3	<.1	1.9	6	.4	6.6
Rela	tive percent	age of c	lifference	9.5	5.8	17	0	6.2	nc	11	0	0	0

			Derl				Com	pound (USG	S NWIS cod	le)			
Station No.	Sample date	Site No.	Repli- cate type	Calcium (00915)	Silica (00955)	Iron (01046)	Chloride (00940)	Magne- sium (00925)	Fluoride (00950)	Sodium (00930)	Manga- nese (01056)	Potas- sium (00935)	Sulfate (00945)
12210700	12-09-97	5	30	11.369	8.877	25.325	1.141	3.326	<.1	1.966	7.353	.5	7.697
			30	11.288	8.842	22.727	1.095	3.337	<.1	1.919	6.488	.4	7.704
Rela	tive percenta	age of d	lifference	<1	<1	11	4.1	<1	nc	2.4	12	22	<1
12113390	02-06-97	6	30	7.4	14	86	2.8	2.1	< 0.1	4.4	28	0.8	4.2
			30	7.3	14	90	3	2.1	<.1	4.3	27	.8	4.2
Rela	tive percenta	age of d	lifference	1.4	0	4.5	6.9	0	nc	2.3	3.6	0	0
12113390	12-17-97	6	30	6.161	10.797	102.52	2.355	1.833	<.1	3.721	16.174	1.37	3.254
12115570	12-17-97	0	30	6.188	10.777	102.32	2.335	1.85	<.1	3.739	16.416	1.37	3.247
Rela	tive percenta	age of d		<1	<1	5.5	1.2	<1	nc	<1	1.5	0	<1
	-	-											
12113375	12-12-95	7	20	11	13	650	5.9	4.2	<.1	7.9	83	2.4	8.7
			20	11	13	650	6.1	4.1	.1	8.1	82	2.3	8.6
Rela	tive percenta	age of d	lifference	0	0	0	3.3	2.4	nc	2.5	1.2	4.3	1.2
12113375	07-15-96	7	10	27	33	700	24	15	.3	33	320	4.1	12
			10	27	33	590	23	15	.3	33	320	4.3	12
Rela	tive percenta	age of d	lifference	0	0	17	4.3	0	0	0	0	4.8	0
12113375	11-20-96	7	30	12	9.9	390	11	4.3	.1	9.1	71	1.9	11
			30	12	9.9	420	11	4.3	.1	9.1	71	1.9	11
Rela	tive percenta	age of d	lifference	0	0	7.4	0	0	0	0	0	0	0
12113375	01-06-98	7	30	8.967	7.662	234.23	4.407	3.037	<.1	4.87	70.732	1.69	5.603
			30	8.995	7.796	245.26	4.335	3.037	<.1	4.898	70.038	1.64	5.463
Rela	tive percenta	age of d	lifference	<1	1.7	4.6	1.6	0	nc	<1	1	3	2.5
12112600	12-12-95	8	20	9.5	13	93	3.9	3.3	.1	6.3	4	1.5	8.5
12112000	12-12-95	0	20	9.4	13	93	3.8	3.3	.1	6.3	4	1.6	8.3
Rela	tive percenta	age of d		1.1	0	0	2.6	0	0	0.5	0	6.5	2.4
12112600	10 16 06	0	20	12	10	05	4.4	5	- 1	5 5	14	16	12
12112600	10-16-96	8	30 30	13	18	95 100	4.4	5	<.1	5.5	14	1.6	13
Rela	tive percenta	age of d		14 7.4	19 5.4	100 5.1	4.4 0	5.3 5.8	<.1 nc	5.9 7	14 0	1.7 6.1	13 0
	r · · ·	0											
12112600	01-06-98	8	30	8.907	11.075	96.029	3.636	3.182	<.1	5.349	7.859	1.46	6.519
Rela	tive percenta	age of d	30 lifference	9.347 4.8	11.61 4.7	100.57 4.6	3.676 1.1	3.34 4.8	<.1 nc	5.629 5.1	8.09 2.9	1.65 12	6.531 <1
Kela	uve percenti	ige of u		т.0	Τ. /	4.0	1.1	т.0	ne	5.1	2.7	12	~1
12108500	12-13-95	9	20	12	18	140	7.3	3.9	.1	7.3	6	5.5	6.9
			20	12	18	130	7.2	4	.1	7.7	5	5.5	6.9
Rela	tive percenta	age of d	lifference	0	0	7.4	1.4	2.5	0	5.3	18	0	0

 Table B5.
 Concentrations of major ions in replicate environmental water samples, Puget Sound Basin, Washington—Continued

			Dauli				Com	pound (USG	iS NWIS cod	le)			
Station No.	Sample date	Site No.	Repli- cate type	Calcium (00915)	Silica (00955)	lron (01046)	Chloride (00940)	Magne- sium (00925)	Fluoride (00950)	Sodium (00930)	Manga- nese (01056)	Potas- sium (00935)	Sulfate (00945)
12108500	08-12-96	9	30	15	19	15	5.2	4.8	<.1	6.4	3	1.8	6.4
			30	15	18	16	5	4.7	<.1	6.3	3	1.8	6.5
Rela	ative percent	age of o	lifference	0	5.4	6.5	3.9	2.1	nc	1.6	0	0	1.6
12108500	07-15-97	9	30	13.833	19.719	167.34	4.423	4.231	< 0.1	6.013	5.413	3.39	5.213
			30	14.329	20.362	175.36	4.65	4.381	<.1	6.209	5.413	3.6	5.15
Rela	ative percent	age of o	lifference	3.5	3.2	4.7	5	3.5	nc	3.2	0	6	1.2
12108500	02-19-98	9	30	13.696	18.996	102.24	4.909	4.42	<.1	6.2	<4	2.8	6.666
			30	13.785	19.107	104	4.877	4.443	<.1	6.2	<4	2.8	6.635
Rela	ative percent	age of o	lifference	<1	<1	1.7	<1	<1	nc	0	nc	0	<1
12128000	06-07-96	11	30	20	29	200	7.8	12	.1	8.2	40	2.4	18
			30	18	26	110	7.3	11	.1	7.6	34	2.2	19
Rela	ative percent	age of o	lifference	10	11	58	6.6	8.7	0	7.6	16	8.7	5.4
12128000	04-07-97	11		19.337	25.74	154.96	7.159	11.463	<.1	8.375	35.42	2.34	19.03
			30	19.724	25.975	157.34	7.231	11.484	<.1	8.331	35.832	2.28	18.914
Rela	ative percent	age of o	lifference	2	<1	1.5	1	<1	nc	<1	1.2	2.6	<1
12128000	03-09-98	11	40	15.814	18.954	131.04	5.016	8.605	<.1	6.253	45.965	1.86	13.893
			40	15.795	18.996	141.32	5.265	8.597	<.1	6.263	46.506	1.83	13.319
Rela	ative percent	age of o	lifference	<1	<1	7.5	4.8	<1	nc	<1	1.2	1.6	4.2
Summary:													
Minir	num percent	age of o	lifference	0	0	0	0	0	0	0	0	0	0
Maxir	num percent	age of o	lifference	10	11	58	11	8.7	0	19	18	40	5.4
Me	dian percent	age of d	lifference	0.8	0.85	6	2.6	1.1	0	1.6	1.2	1.6	0.25

 Table B5.
 Concentrations of major ions in replicate environmental water samples, Puget Sound Basin, Washington—Continued

Table B6. Concentrations of nutrients in replicate environmental water samples for the Puget Sound Basin study unit, Washington

[Replicate types: 10-concurrent, 20-sequential, 30-split, 40-split-concurrent; compound values are in milligrams per liter and dissolved unless otherwise noted; USGS NWIS, U.S. Geological Survey National Water Information System; <, less than; --, not analyzed; nc, not calculated; relative percentage of difference = $|R1 - R2| \times 100$, where R1 = sample 1 result and R2 = sample 2 result]

$$\left(\frac{R1+R2}{2}\right)$$

						Com	pound (USG	S NWIS cod	le)		
Station No.	Sample date	Site No.	Replicate type	Phos- phorus, total (00665)	Phosphorus (00666)	Ortho- phosphate phosphorus (00671)	Nitrite, as N (00613)	Nitrite- plus- nitrate, as N (00631)	Ammonia, as N (00608)	Ammonia- plus- organic, as N, total (00625)	Ammonia- plus- organic, as N (00623)
12061500	01-07-98	1	30	0.019	0.014	0.012	< 0.01	0.087	< 0.02	< 0.1	< 0.1
			30	.024	.014	.011	<.01	.09	<.02	<.1	<.1
	Relative	percentage	of difference	23	0	8.7	nc	3.4	nc	nc	nc
12056500	09-17-97	2	30	<.01	<.01	<.01	<.01	.06	<.015	<.2	<.2
			30	.016	<.01	<.01	<.01	.061	<.015	<.2	<.2
	Relative	percentage	of difference	nc	nc	nc	nc	1.7	nc	nc	nc
12056500	01-07-98	2	30	<.01	<.01	.02	<.01	<.05	<.02	<.1	<.1
			30	.026	.02	.011	<.01	<.05	<.02	<.1	<.1
	Relative	percentage	of difference	nc	nc	58	nc	nc	nc	nc	nc
12213140	02-20-96	3	30	.09	<.01	.01	.01	.52	.05	<.2	<.2
			30	.05	<.01	.02	.01	.51	.06	<.2	<.2
	Relative	percentage	of difference	57	nc	67	0	1.9	18	nc	nc
12213140	02-14-97	3	30	.06	<.01	<.01	.01	.93	.06	<.2	<.2
			30	.07	<.01	<.01	.02	.94	.07	.2	<.2
	Relative	percentage	of difference	15	nc	nc	67	1.1	15	nc	nc
12213140	11-04-97	3	30	.151	.021	.011	<.01	.257	<.02	.237	<.1
			30	.162	.014	.023	<.01	.283	<.02	.236	.102
	Relative	percentage	of difference	7	40	7.6	nc	9.6	nc	.4	nc
12212100	07-09-96	4	30	<.01	<.01	.01	.02	2.5	.04	.2	.2
			30	<.01	<.01	.02	.02	1.5	.03	<.2	<.2
	Relative	percentage	of difference	nc	nc	67	0	50	29	nc	nc
12212100	04-08-97	4	30	.01	<.01	<.01	.02	3.9	.09	.3	.2
			30	.02	<.01	<.01	.02	3.9	.08	.3	<.2
	Relative	percentage	of difference	67	nc	nc	0	0	12	0	nc
12212100	02-11-98	4	30	.06	<.01	.017	.02	3.555	.084	.466	.334
			30	.063	<.01	.013	.019	3.547	.08	.41	.272
	Relative p	percentage of	of difference	4.9	nc	27	5.1	<1	4.9	13	2.5
12210700	02-20-96	5	30	.05	<.01	<.01	<.01	.21	<.015	<.2	<.2
			30	.04	<.01	<.01	<.01	.21	<.015	<.2	<.2
	Relative p	percentage of	of difference	22	nc	nc	nc	0	nc	nc	nc

Table B6. Concentrations of nutrients in replicate environmental water samples, Puget Sound Basin, Washington—Continued

	Sample date					Com	pound (USG	S NWIS cod	e)		
Station No.	•	Site No.	Replicate type 30	Phos- phorus, total (00665)	Phosphorus (00666)	Ortho- phosphate phosphorus (00671)	Nitrite, as N (00613)	Nitrite- plus- nitrate, as N (00631)	Ammonia, as N (00608)	Ammonia- plus- organic, as N, total (00625)	Ammonia- plus- organic, as N (00623)
12210700	01-08-97	5	30	< 0.01	< 0.01	< 0.01	0.02	0.33	0.03	<0.2	< 0.2
			30	<.01	<.01	<.01	.01	<.05	.05	<.2	<.2
	Relative	percentage	of difference	nc	nc	nc	67	nc	50	nc	nc
12210700	03-11-97	5	30	<.01	<.01	<.01	<.01	.23	<.015	<.2	<.2
			30	<.01	<.01	<.01	<.01	.23	<.015	<.2	<.2
	Relative	percentage	of difference	nc	nc	nc	nc	0	nc	nc	nc
12210700	12-09-97	5	30	.01	<.01	<.01	<.01	.209	<.02	<.1	<.1
			30	<.01	<.01	<.01	<.01	.219	<.02	<.1	<.1
	Relative	percentage	of difference	nc	nc	nc	nc	4.7	nc	nc	nc
12113390	02-06-97	6	30	.05	<.01	.01	.03	.53	.05	.4	<.2
		-	30	.08	.01	.01	.02	.5	.05	.2	<.2
	Relative	percentage	of difference	46	nc	0	40	5.8	0	67	nc
12113390	12-17-97	6	30	.155	.038	.054	<.01	.661	.049	.626	.273
		-	30	.188	.043	.053	<.01	.663	.05	.684	.252
	Relative	percentage	of difference	19	12	1.9	nc	<1	2	8.9	8
12113375	12-12-95	7	20	.1	.05	.04	<.01	.7	.06	.5	.4
	/ •		20	.1	.05	.05	<.01	.7	.07	.5	.4
	Relative	percentage	of difference	0	0	22	nc	0	15	0	0
12113375	07-15-96	7	10	.129	.024	.05	.056	.633	.236	.539	.437
12110070	0, 10 ,0		10	.131	.022	.042	.055	.629	.236	.57	.552
	Relative	percentage	of difference	1.5	8.7	17	1.8	<1	0	5.6	23
12113375	01-06-98	7	30	.101	.02	.026	<.01	.453	<.02	.446	.284
			30	.102	.017	.023	<.01	.457	.026	.468	.272
	Relative	percentage	of difference	1	16	12	nc	<1	nc	4.8	4.3
12112600	12-12-95	8	20	.03	<.01	.02	<.01	1.4	<.015	.3	.2
			20	.03	<.01	.01	<.01	1.4	<.015	.3	.3
	Relative	percentage	of difference	0	nc	67	nc	0	nc	0	40
12112600	10-16-96	8	30	.04	.04	.03	.02	.68	.06	.4	.3
		-	30	.08	.06	.03	.01	.69	.06	.3	.2
	Relative p	percentage of	of difference	67	40	0	67	1.5	0	29	40
12112600	01-06-98	8	30	.037	.021	.02	<.01	.981	<.02	.401	.225
	51 00 70	5	30	.028	.012	.022	<.01	.956	<.02	.362	.273
	Relative r	hercentage (of difference	28	54	9.5	nc	2.6	nc	1.2	19

 Table B6.
 Concentrations of nutrients in replicate environmental water samples, Puget Sound Basin, Washington—Continued

						Com	pound (USG	S NWIS cod	e)		
Station No.	Sample date	Site No.	Replicate type	Phos- phorus, total (00665)	Phosphorus (00666)	Ortho- phosphate phosphorus (00671)	Nitrite, as N (00613)	Nitrite- plus- nitrate, as N (00631)	Ammonia, as N (00608)	Ammonia- plus- organic, as N, total (00625)	Ammonia- plus- organic, as N (00623)
12108500	12-13-95	9	20	0.35	0.36	0.27	0.04	2.9	0.21	0.8	1
			20	.34	.33	.26	.04	2.9	.2	.8	.9
	Relative	percentage	of difference	2.9	8.7	3.8	0	0	4.9	0	1.5
12108500	08-12-96	9	30	.02	.06	.06	.01	1.6	.03	<.2	<.2
			30	.04	.05	.06	.01	1.7	.03	<.2	<.2
	Relative	percentage	of difference	67	18	0	0	6.1	0	nc	nc
12108500	07-15-97	9	30	.234	.168	.16	.061	1.735	.026	.538	.475
			30	.26	.166	.164	.06	1.751	.023	.519	.239
	Relative	percentage	of difference	1.5	1.2	2.5	1.7	<1	12	3.6	66
12108500	02-19-98	9	30	.131	.089	.08	.011	2.773	.031	.421	.282
			30	.127	.091	.08	.011	2.767	.037	.434	.277
	Relative	percentage	of difference	3.1	2.2	0	0	<1	18	3	1.8
12128000	06-07-96	11	30	.04	.04	.02	.02	1.2	<.015	.3	<.2
			30	.06	.05	.03	.01	1.3	<.015	.3	<.2
	Relative	percentage	of difference	40	22	40	67	8	nc	0	nc
12128000	04-07-97	11	30	.03	.01	.02	<.01	1.3	<.015	<.2	<.2
			30	.04	<.01	.02	<.01	1.3	<.015	<.2	<.2
	Relative	percentage	of difference	29	nc	0	nc	0	nc	nc	nc
12128000	03-09-98	11	40	.049	.021	.024	<.01	1.134	.03	.475	.247
			40	.04	.017	.024	<.01	1.133	.028	.293	.196
	Relative	percentage	of difference	2.2	21	0	nc	<1	6.9	47	23
12128000	03-09-98	11	40	.042	.015	.024	<.01	1.113	.028	.307	.189
			40	.041	.02	.026	<.01	1.126	.031	.29	.191
	Relative	percentage	of difference	2.4	29	8	nc	1.2	1.2	5.7	1.1
Summary:											
	Minimum	percentage	of difference	0	0	0	0	0	0	0	0
	Maximum	percentage	of difference	67	54	7.6	67	50	50	67	66
	Median	percentage	of difference	19	16	9.1	1.75	0.9	10	4.8	19

Table B7. Concentrations of organic carbon in replicate environmental water samples for the Puget Sound Basin study unit, Washington

[Compound detection values are in milligrams per liter. USGS NWIS, U.S. Geological Survey National Water Information System; <, less than; --, not analyzed; nc, not calculated; relative percentage of difference = $\frac{|R1 - R2|}{\left(\frac{R1 + R2}{2}\right)} \times 100$, where R1 = sample 1 result and R2 = sample 2 result]

				Compound (US	SGS NWIS code)
Station No.	Sample date	Site No.	Replicate type	Carbon, dissolved (00681)	Carbon, suspended (00689)
12056500	04-11-97	2	concurrent	0.6	nc
				.4	0.1
	Relative percer	ntage of difference		40	nc
12056500	09-17-97	2	split	2.1	.3
12050500	0, 11, ,1	-	spin	2.2	.3
	Relative percer	ntage of difference		4.7	0
12213140	05-07-97	2	concurrent	2.5	7
12213140	05-07-97	3	concurrent	2.5	.7 .5
	Polotivo poroo	ntage of difference		4.1	.5 33
	Relative percer	hage of difference		4.1	55
12213140	11-04-97	3	split	3.3	1.3
				3.6	1.3
	Relative percer	ntage of difference		8.7	0
12212100	07-09-96	4	split	2.2	.4
			1	2.2	.4
	Relative percer	ntage of difference		0	0
12212100	04-08-97	4	split	2.6	.5
12212100	04-08-97	+	spin	2.6	.5
	Relative percer	ntage of difference		0	0
12212100	05-06-97	4	oononmont	6	1.7
12212100	03-00-97	4	concurrent	5.5	1.7
	Relative percer	ntage of difference		8.7	1.9
12212100	02-11-98	4	split	3.1	1.5
	Dalation manage			3.1	1.4
	Relative percer	ntage of difference		0	6.9
12210700	01-08-97	5	split	2.3	.4
				2.3	.5
	Relative percer	ntage of difference		0	22
12210700	12-09-97	5	split	1.1	.2
				1	.2
	Relative percer	ntage of difference		9.5	0
12113390	09-12-96	6	concurrent	1.4	.5
		-		1.4	.5
				1.4	.6
Re	elative percentage of d	ifference R1 & R2		0	0
	percentage of differen			0	18
12113390	05-16-97	6	concurrent	1.3	.5
12113370	05-10-27	0	concurrent	1.5	.5
	Relative percer	ntage of difference		8	0

				Compound (USGS NWIS code)			
Station No.	Sample date	Site No.	Replicate type	Carbon, dissolved (00681)	Carbon, suspende (00689)		
12113390	12-17-97	6	split	3.3	2.6		
				3.3	2.1		
	Relative percent	ntage of difference		0	21		
12113375	07-15-96	7	concurrent	4.9	0.7		
				5.3	.6		
	Relative percent	ntage of difference		7.8	15		
12113375	01-03-97	7	concurrent	4	.4		
				4.1	.4		
	Relative percent	ntage of difference		2.5	0		
12113375	01-06-98	7	split	4.3	1.4		
			-	4.4	1.2		
	Relative percent	ntage of difference		2.3	15		
12112600	10-16-96	8	split	4.2	.3		
			I.	4.2	.1		
	Relative percent	ntage of difference		0	100		
12112600	01-06-98	8	split	5.1	1.2		
			*	5	1.3		
	Relative percent	ntage of difference		2	8		
12108500	08-12-96	9	split	1.2	.3		
				1.3	.2		
	Relative percent	ntage of difference		8	40		
12108500	11-15-96	9	concurrent	9.6	.6		
				9.7	.6		
	Relative percent	ntage of difference		1	0		
12108500	02-19-98	9	split	3.9	1		
				3.8	1		
	Relative percent	ntage of difference		2.6	0		
12103380	07-14-97	10	concurrent	0.7	.2		
				.7	.2		
	Relative percent	ntage of difference		0	0		
12128000	06-07-96	11	split	2.5	.4		
				2.4	.4		
	Relative percent	ntage of difference		4.1	0		
12128000	04-07-97	11	split	2.8	.3		
				2.9	.3		
	Relative percent	ntage of difference		3.5	0		
Summary:							
		ntage of difference		0	0		
		ntage of difference		40	100		
	Median percer	ntage of difference		2.5	0		

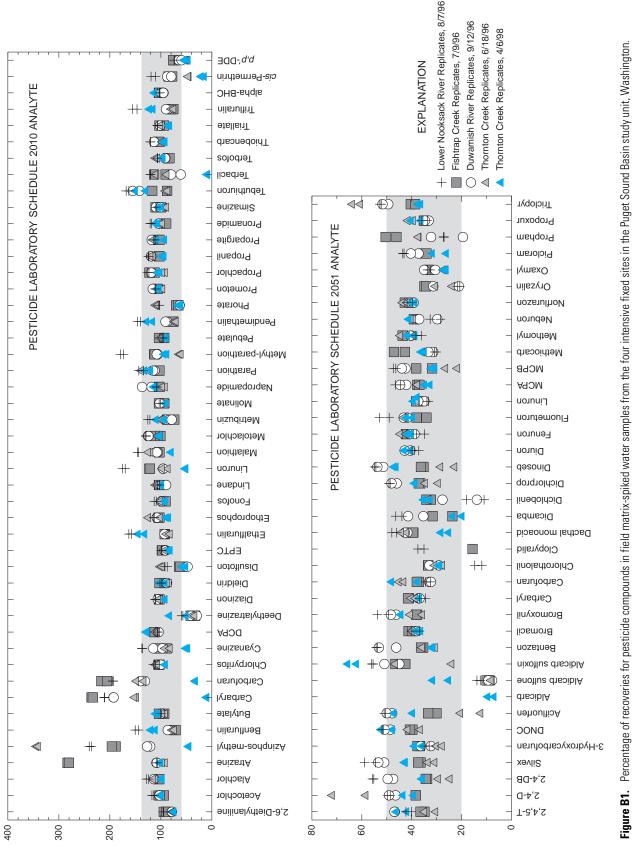
 Table B7.
 Concentrations of organic carbon in replicate environmental water samples, Puget Sound Basin, Washington—Continued

 Table B8.
 Concentrations of pesticide compounds detected in replicate environmental water samples for the Puget Sound Basin study unit,

 Washington

[Compound detection values are in micrograms per liter. USGS NWIS, U.S. Geological Survey National Water Information System; <, less than; ^E, estimated; nc, not calculated; relative percentage of difference = $\frac{[R1 - R2]}{\left(\frac{R1 + R2}{2}\right)}$ ¥ 100, where R1 = sample 1 result and R2 = sample 2 result]

	Sample date	Site No.	Replicate type	Compound (USGS NWIS code)								
Station No.				Atrazine (39632)	Deethyl- atrazine (04040)	Diazinon (39572)	EPTC (82668)	Metol- achlor (39415)	Prometon (04037)	Sima- zine (04035)	Tebu- thiuron (82670)	Dichlo- benil (49303)
12212100	04-08-97	4	split	0.032	E0.006	< 0.002	< 0.002	0.004	E0.004	0.008	0.019	<1.2
				.031	^E .006	^E .002	<.002	^E .004	^E .004	.008	.019	<1.2
	Relative p	ercentage o	of difference	3.2	0	nc	nc	0	0	0	0	nc
12212100	06-10-97	4	split	.0171	^E .00305	^E .0035	^E .00146	^E .0024	^E .005	.0111	<.01	<1.2
				.0218	^E .00278	^E .00234	^E .00195	<.002	^E .0055	.0132	.0122	<1.2
	Relative percent age of difference			24	9.3	40	29	nc	9.5	17	nc	nc
12128000	04-07-97	11	split	^E .002	^E .002	^E .003	<.002	<.002	0.019	^E .003	<.01	<1.2
				^E .002	^E .002	^E .002	<.002	<.002	^E .018	^E .003	<.01	<1.2
	Relative p	ercentage	of difference	0	0	40	nc	nc	5.4	0	nc	nc
12128000	03-09-98	11	split- concurrent	<.001	<.002	.0309	<.002	<.002	.02	.011	<.01	^E 0.1
				<.001	<.002	.0245	<.002	<.002	.0194	.011	<.01	^E .08
	Relative p	ercentage o	of difference	nc	nc	23	nc	nc	3	0	nc	22
12128000	03-09-98	11	split- concurrent	<.001	<.002	.026	<.002	<.002	.0181	.0103	<.01	^E .08
				<.001	<.002	.0241	<.002	<.002	^E .0179	.0101	<.01	^E .12
	Relative p	ercentage o	of difference	nc	nc	7.6	nc	nc	1.1	2	nc	40
Summary:												
Ν	Ainimum p	ercentage o	of difference	0	0	7.6	29	0	0	0	0	22
Ν	laximum p	ercentage o	of difference	24	9.3	40	29	0	9.5	17	0	40
	Median p	ercentage o	of difference	3.2	0	31	29	0	3	0	0	31



АИАLYTE RECOVERY, IN PERCENT

Volatile organic compound	Mean (percent)	Standard deviation (percent)	Number of samples
1,1,1-Trichloroethane	98	3	8
1,1-Dichloroethene	92	8	8
1,2-Dichloroethane	101	10	8
1,4-Dichlorobenzene	76	11	8
Bromodichloromethane	89	5	8
Bromoform	71	6	8
Chloroethene	71	26	8
Dibromochloromethane	82	5	8
Ethylbenzene	89	3	8
Methyl tert-butyl ether	86	3	8
Tetrachloroethene	88	10	8
Tetrachloromethane	99	6	8
Trichloroethene	90	7	8

Table B9. Summary of percentage of mean recoveries from fieldmatrix-spike volatile organic compound analyses for the Puget Sound Basin study unit, Washington

Table B10. Summary of surrogate compound recoveries in filtered water samples for pesticide analyses for the Puget Sound Basin study unit, Washington

Table B11. Summary of surrogate compound recoveries in whole water samples for volatile organic compound analyses for the Puget Sound Basin study unit, Washington

[Values are percentages. USGS NWIS, U.S. Geological Survey National Water Information System; nc, not calculated]

[Values are percentages. USGS NWIS, U.S. Geological Survey National Water Information System; nc, not calculated]

No.	Number of samples		Compound (USGS NWIS code)							Compound (USGS NW		/IS code)
			BDMC (99835)	Diazinon <i>-d</i> 10 (91063)	Terbuthy- lazine (91064)	Alpha- HCH- <i>d</i> 6 (91065)	Station No (Site No.)	Number of samples		1,2- dichloro- ethane- <i>d</i> 4 (99832)	Toluene- <i>d</i> 8 (99833)	1,4-bromo fluoro- benzene (99834)
12213140	22	Mean	89	104	112	99						
(3)		Standard	12	12	13	13	12213140	22	Mean	89	104	112
12212100	32	deviation Mean	91	105	110	101	(3)		Standard deviation	12	12	13
(4)	52	Standard	11	105	110	13	12212100	32	Mean	91	105	110
(+)		deviation	11	12	14	15	(4)	02	Standard	11	12	14
12113390	24	Mean	88	108	120	107			deviation			
(6)		Standard deviation	7.2	24	26	24	12113390 (6)	24	Mean Standard	88 7.2	108 24	120 26
12128000	46	Mean	95	108	112	107			deviation			
(11)		Standard	14	9.8	13	13	12128000	46	Mean	95	108	112
()		deviation					(11)		Standard	14	9.8	13
12113375	2	Mean	nc	nc	nc	nc			deviation			
(7)		Standard deviation	nc	nc	nc	nc	12113375 (7)	2	Mean Standard	nc nc	nc nc	nc nc
All	126	Mean	92	106	113	104			deviation			
stations	120	Standard	14	100	16	16	All	126	Mean	92	106	113
Sutions		deviation	11		10	10	stations		Standard deviation	14	14	16

APPENDIX C. NUTRIENT LOAD ESTIMATION

The regression equations generated by the Loadest2 computer program and indicated to best fit the calibration data are listed for each of the 11 sites in table C1 for total nitrogen loads, table C2 for total phosphorus loads, table C3 for dissolved orthophosphate phosphorus (orthophosphate) loads, and table C4 for suspended-sediment loads. Except for the NF Skokomish, Newaukum, and the upper Green, all regression equations to estimate total nitrogen loads contained the sine and cosine functions to account for the seasonality in the data sets, which indicated that variation in the concentration data was great enough that it could not be explained by streamflow alone. Only two of the equations to estimate phosphorus loads included the seasonality terms and these were for the lower Nooksack and Thornton. This indicated that, for most of the sites, most of the variation in phosphorus concentrations was explained by streamflow. For orthophosphate, seasonality terms were in the equations for 5 of 10 sites; the terms were not in equations for the lower Nooksack, Fishtrap, Duwamish, Newaukum, and upper Green. For suspended sediment, the seasonality terms were included in four equations-for the NF Skokomish, upper and lower Nooksack, and Newaukum. Many of the regression equations also included terms such as the log-normal streamflow-squared term $[\ln(Q)^2]$ to help fit the equation to the calibration data.

All nutrient load estimates were calibrated with the daily streamflow value on the day of sample collection except for one-the phosphorus load in the upper Nooksack. Although some investigators prefer daily streamflow for estimating daily loads, the use of instantaneous streamflow is also acceptable (Charles Crawford, USGS, written commun., 1999). In the case of the upper Nooksack, instantaneous streamflows at the time of sample collection were used in the calibration file because these values lowered the standard deviation of the annual average load of phosphorus from 66 to 46 percent, the average percent difference between measured and predicted daily loads from 333 to 309 percent, and the difference between measured and predicted annual load from 81 to -15 percent (table C2). Instantaneous streamflows

rather than the daily streamflows at the time of sample collection were also used in the calibration files for suspended-sediment load estimations at the upper Nooksack, Springbrook, and Thornton because standard deviations (SDs) and percent differences were improved (table C4).

In general, SDs for annual average nitrogen-load estimates were smaller than for phosphorus and orthophosphate load estimates. Sites having data sets with low concentrations and many observations censored at the MRL typically had large SDs. For example, the nitrogen data set for the upper Green River was 42 percent censored and the standard deviation was 40 percent of the load estimate (table C1). Excluding the upper Green, SDs of the annual average nitrogen loads ranged from 3 to 18 percent. For phosphorus, SDs ranged from about 9 to 73 percent including those of sites with greatly censored data sets (Skokomish and NF Skokomish) (table C2). The overall censoring rate for nitrogen is lower than for the phosphorus species partly because of the construction of the calibration data sets; specifically, if one of the nutrient parameters (00625 and 00631) used to calculate total nitrogen (parameter 00600) was missing (censored at the MRL), the total nitrogen was estimated to be equal to the sum of the remaining forms of nitrogen detected in the sample. Thus, for example, for an analysis with organic nitrogen-plus-ammonia (parameter 00625) censored at the MRL, but with a value reported for nitrite-plusnitrate (parameter 00631), a value of total nitrogen equal to the nitrite-plus-nitrate concentration was used in the calibration data set for load estimation. If ammonia was also present, the sum of the ammonia and nitrite-plus-nitrate nitrogen concentrations was used. For some sites, such as the NF Skokomish, the substitution estimate for the total nitrogen parameter was a large part of the data set; at other sites, such as Springbrook and Thornton Creeks, all the nitrogen forms necessary for calculating total nitrogen by the algorithms of the USGS database were present for many of the samples. If no nitrogen forms were present to substitute, then total nitrogen was set to less than 0.05 mg/L, which is the reporting level for the typically dominant form of nitrogen in surface water, nitriteplus-nitrate nitrogen.

For all nutrient load estimates, the maximum likelihood estimation (MLE) method was selected over the linear attribution estimation (LAE) method because the data sets contained little or no censored data and the MLE and the LAE produced essentially the same results. For suspended-sediment loads, however, the degree of censoring affected the choice of load estimation method. Loads computed with the LAE method use a bias-transformation correction factor that is computed from the residuals of the rating curve regression. When a value is censored, the residual is unknown. When a large percentage of the data are censored, the transformation factor will be biased, resulting in a biased estimate of the mean load, whereas the MLE method does not have this limitation (Charles Crawford, USGS, written commun., 1999). Thus, the MLE was favored for the load estimates when more than 20 percent of a data set was censored. Predictions of the concentration percentiles using the MLE also compared better with the concentration percentiles of the actual data than those using the LAE.

For suspended-sediment load estimates, the MLE method was selected for 6 of the 11 sites and the LAE method for the remaining 5 sites (table C4). The highest rate of censoring (27 percent) was for the NF Skokomish data set. Except for the upper Green, SDs for average annual sediment loads ranged from 17 percent to 56 percent. The SD for the upper Green was greater than 100 percent, indicating the results should be viewed with caution and suggesting that further data collection is needed to better define the relation of suspended sediment and steamflow at this site. If censoring rates were not a factor, and if the normality test statistic and the p-value indicated that the regression residuals followed a non-normal distribution, the LAE method was selected (Charles Crawford, USGS, written commun., 1999). Thus, for the upper Nooksack, Duwamish, Springbrook, Newaukum, and Thornton, the suspended-sediment load was estimated with the LAE method.

Figures C1 through C11 show, for each of the 11 fixed sites, predicted daily loads and measured loads of total nitrogen, phosphorus, and orthophosphate over time. Figure C12 shows the same type of information for suspended sediment. These figures include scatterplots of the calibration data used by the loadestimation program showing concentration as a function of daily or instantaneous streamflow. Percent differences between measured and predicted daily loads of total nitrogen were large for some sites, ranging from an average of 1.6 percent at Fishtrap to 125 percent at the NF Skokomish (table C1). However, percent differences between predicted and measured loads on an annual basis were much smaller, ranging from -26 to less than 1 percent, indicating that, on average, the estimated annual loads were reasonable.

Predicted annual loads of phosphorus and orthophosphate also agreed reasonably well with measured loads for about half the sites. At Skokomish, Fishtrap, upper Nooksack, Big Soos, and Thornton, the equations tended to overpredict daily loads of phosphorus or orthophosphate during parts of water year 1997. As with nitrogen loads, the predicted and measured daily loads varied greatly, with average differences ranging from 14 to 309 percent for phosphorus and from -9 to 130 percent for orthophosphate. Except for the NF Skokomish phosphorus loads, though, the predicted annual loads agreed reasonably well with measured annual loads, with differences ranging from -23 to 21 percent for phosphorus and from -22 to 31 percent for orthophosphate (see <u>tables C2</u> and <u>C3</u>). For the NF Skokomish, there was a 74 percent difference between the measured and predicted annual phosphorus load, which was probably due to low concentrations and a highly censored (73 percent) data set.

Predicted annual loads of suspended sediment agreed reasonably well with measured loads for most sites. For the Skokomish, NF Skokomish, Duwamish, and Big Soos, the equations tended to overpredict the suspended-sediment loads. As with the nutrients, average percent differences between measured and predicted daily suspended-sediment loads were sometimes large, ranging from 11 percent at Springbrook to 284 percent at the Skokomish. Percent differences between predicted measured annual loads were smaller for all sites, ranging from -48 to 88 percent (<u>table C4</u>). The load estimates for the Skokomish, NF Skokomish, Duwamish, Big Soos, upper Green, and Thornton should be viewed with caution because of the large standard deviations, the extreme variability between measured and predicted daily loads, and the large percent difference between measured and predicted annual loads.

For Fishtrap and Thornton Creeks, the daily streamflow data sets were not complete for water year 1996. Streamgages installed at these sites did not begin recording daily flows until late May 1996 and March 1996, respectively. Thus all annual loads estimated for these two sites are based on the 2 years of complete streamflow record, 1997 and 1998, available during the study. Table C1. Total nitrogen loads, standard deviations, and regression equations for load estimates for surface-water sites in the Puget Sound Basin study unit, Washington

[Annual load: Annual load, from the regression equation for the simulation period (10/01/95 - 09/30/98); calculated as annual load, in tons = annual average load, in pounds per day, times 365 days, divided by 2000. Average percentage of difference between measured and predicted daily loads: Measured daily loads, in pounds, are calculated by multiplying the constituent concentration and instantaneous or daily streamflow measured on the day of sample collection. Predicted daily loads, in pounds, are the regression-equation results for the days of sample collection. Measured and predicted loads: Measured load, in tons per year, is estimated by multiplying the simple average of the measured daily loads by 365 days. Predicted load, in tons per year, is estimated by multiplying the simple average of the days of sample collection by 365 days. Precentage of difference = [(predicted - measured)/measured] * 100; In, natural logarithm; Q, streamflow in cubic feet per second; sin, sine; cos, cosine; dectime, time in fractional years; --, no value; MLE, maximum likelihood estimate; dload, daily load, in pounds]

Site name (Site No.)	Annual Ioad (tons)	Annual load standard deviation, in tons, and (as percentage)	Average percentage of difference between measured and predicted daily loads (pounds)	<u>Measured</u> and predicted loads, in tons per year, and (percentage of difference)	Regression equation	Censored data (percent)
Skokomish River (1)	210	29 (14)	49	<u>640;</u> 570 (-10)	MLE: $\ln(dload) = 6.3877 + 1.0366 \ln(Q)$ + 0.14968 $\ln(Q)^2$ - 0.21928sin(dectime) + 0.35471cos(dectime)	8
North Fork Skokomish River (2)	49	8.9 (18)	125	<u>89;</u> 91 (0.2)	MLE: ln(dload)=5.143 + 1.0776ln(Q)	36
Lower Nooksack River (3)	3,200	220 (6.9)	14	<u>5,850;</u> 5,900 (0.8)	MLE: ln(dload)=9.2020 + 1.2585ln(Q) + 0.10488sin(dectime) + 0.68187cos(dectime)	0
Fishtrap Creek (4)	¹ 330	¹ 10 (3.0)	1.6	<u>480;</u> 450 (-6.4)	MLE: ln(dload)=7.6999 + 1.0939ln(Q) - 0.06444ln(Q) ² + 0.15458sin(dectime) + 0.11826cos(dectime) - 0.09019dectime	0
Upper Nooksack River (5)	1,600	200 (12.5)	32	<u>3,400;</u> 2,900 (-16)	MLE: ln(dload)=8.2301 + 1.4532ln(Q) - 0.18879sin(dectime) + 0.52754cos(dectime)	0
Duwamish River (6)	1,300	150 (12)	34	<u>2,100;</u> 2,000 (-5.0)	MLE: ln(dload)=8.3513 + 0.8101ln(Q) + 0.16238ln(Q) ² + 0.29708sin(dectime) +0.46756cos(dectime)	0
Springbrook Creek (7)	44	1.3 (3.0)	1.7	<u>70;</u> 71 (1.3)	MLE: ln(dload)=5.5426 + 0.87089ln(Q) + 0.055932sin(dectime) + 0.090628cos(dectime) - 0.065345dectime	0
Big Soos Creek (8)	200	12 (6.0)	5.2	<u>310;</u> 300 (-2.3)	MLE: ln(dload)=7.1444 + 0.095208ln(Q) + 0.086982sin(dectime) + 0.41256cos(dectime) - 0.14288dectime	0
Newaukum Creek (9)	210	11 (5.2)	6.2	<u>308;</u> 310 (0.6)	MLE: ln(dload)=7.106 + 1.1741ln(Q) - 0.093713ln(Q) ²	0
Upper Green River (10)	6.0	2.4 (40)	105	<u>8.0;</u> 6.0 (-26)	MLE: ln(dload)=2.5669 + 1.1906ln(Q)	42
Thornton Creek (11)	¹ 20	¹ 0.9 (4.5)	7.5	<u>24.8;</u> 25.1 (1.5)	MLE: ln(dload)=4.3827 + 1.0855ln(Q) + 0.12241sin(dectime) - 0.032546cos(dectime)	0

¹ Calculated from load estimates for the complete water years 1997 and 1998 only.

Table C2. Total phosphorus loads, standard deviations, and regression equations for load estimates for surface-water sites in the Puget Sound Basin study unit, Washington

[Annual load: Annual load, from the regression equation for the simulation period (10/01/95 - 09/30/98); calculated as annual load, in tons = annual average load, in pounds per day, times 365 days, divided by 2000. Average percentage of difference between measured and predicted daily loads: Measured daily loads, in pounds, are calculated by multiplying the constituent concentration and instantaneous or daily streamflow measured on the day of sample collection. Predicted daily loads, in pounds, are the regression-equation results for the days of sample collection. Measured and predicted loads: Measured load, in tons per year, is estimated by multiplying the simple average of the measured daily loads by 365 days. Predicted load, in tons per year, is estimated by multiplying the simple average of daily loads predicted for the days of sample collection by 365 days. Percentage of difference = [(predicted - measured)/measured] * 100; In, natural logarithm; Q, streamflow in cubic feet per second; sin, sine; cos, cosine; dectime, time in fractional years; -, no value; MLE, maximum likelihood estimate; dload, daily load, in pounds]

Site name (Site No.)	Annual Ioad (tons)	Annual load standard deviation, in tons, and (as percentage)	Average percentage of difference between measured and predicted daily loads (pounds)	<u>Measured</u> and predicted loads, in tons per year, and (percentage of difference)	Regression equation	Censored data (percent)
Skokomish River (1)	170	68 (40)	270	<u>630;</u> 710 (12)	MLE: ln(dload) = 4.7457 + 2.1801ln(Q)	41
North Fork Skokomish River (2)	15	11 (73)	55	<u>34;</u> 59 (74)	$\begin{array}{l} MLE: \ln(dload) = 2.1177 + 1.4814(Q) \\ + 0.48016 \ln(Q)^2 \end{array}$	73
Lower Nooksack River (3)	890	200 (22)	54	<u>3,700;</u> 2,900 (-22)	MLE: $ln(dload)=6.8581 + 3.1232ln(Q)$ - 0.36967ln(Q) ² - 0.44919sin(dectime) + 0.052735cos(dectime)	10
Fishtrap Creek (4)	¹ 11	¹ 2.0(18)	62	<u>18;</u> 17 (-6.0)	MLE: $\ln(dload)=3.3276 + 2.0133\ln(Q) + 0.17042\ln(Q)^2$	7
Upper Nooksack River (5)	720	330 (46)	309	<u>2,200;</u> 1,900 (-15)	² MLE: $\ln(dload)=5.799 + 3.6862\ln(Q)$ - 0.54765 $\ln(Q)^2$	34
Duwamish River (6)	190	31 (16)	41	<u>430;</u> 380 (-12)	$\begin{array}{l} MLE: ln(dload) = 6.1382 + 1.4551ln(Q) \\ + 0.24499ln(Q)^2 \end{array}$	0
Springbrook Creek (7)	6.9	0.6 (8.7)	14	<u>12;</u> 11 (-4.3)	MLE: ln(dload)=3.5589 + 1.0474ln(Q) - 0.085863ln(Q) ²	0
Big Soos Creek (8)	9.5	2.0 (21)	81	<u>22;</u> 17 (-23)	MLE: ln(dload)=3.4184 + 1.5624ln(Q)	11
Newaukum Creek (9)	27	6.0 (22)	58	<u>31;</u> 38 (21)	MLE: ln(dload)=4.1531 + 1.8088ln(Q)	0
Upper Green River (10)	³ 2-2.6	_	-	<u>2.2;</u> – (–)	_	75
Thornton Creek (11)	¹ 1.5	¹ 0.4 (27)	100	<u>2.7;</u> 3.0 (14)	MLE: ln(dload)=1.1371 + 1.8727ln(Q) + 0.00155sin(dectime) - 0.41633cos(dectime)	02

¹Calculated from load estimates for the complete water years 1997 and 1998 only.

²Regression equation calibrated with instantaneous streamflow (parameter 00061) in place of daily streamflow (parameter 00060).

³Beale ratio estimate (Crawford, 1996).

 Table C3.
 Dissolved orthophosphate phosphorus loads, standard deviations, and regression equations for load estimates for surface-water sites in the

 Puget Sound Basin study unit, Washington

[Annual load: Annual load, from the regression equation for the simulation period (10/01/95 - 09/30/98); calculated as annual load, in tons = annual average load, in pounds per day, times 365 days, divided by 2000. Average percentage of difference between measured and predicted daily loads: Measured daily loads, in pounds, are calculated by multiplying the constituent concentration and instantaneous or daily streamflow measured on the day of sample collection. Predicted daily loads, in pounds, are the regression-equation results for the days of sample collection. Measured and predicted loads: Measured load, in tons per year, is estimated by multiplying the simple average of the measured daily loads by 365 days. Predicted load, in tons per year, is estimated by multiplying the simple average of the days of sample collection by 365 days. Predicted load, in tons per year, is estimated by multiplying the simple average of sample collection by 365 days. Percentage of difference = [(predicted - measured)/measured] * 100; ln, natural logarithm; Q, streamflow in cubic feet per second; sin, sine; cos, cosine; dectime, time in fractional years; --, no value; MLE, maximum likelihood estimate; dload, daily load, in pounds]

Site name (Site No.)	Annual load (tons)	Annual load standard deviation, in tons, and (as percentage)	Average percentage of difference between measured and predicted daily loads (pounds)	<u>Measured</u> and predicted loads, in tons per year, and (percentage of difference)	Regression equation	Censored data (percent)
Skokomish River (1)	16	1.8 (11)	37	<u>45;</u> 44 (-2.1)	MLE: $ln(dload) = 3.5323 + 0.76949ln(Q)$ + 0.24054ln(Q) ² - 0.045632sin(dectime) + 0.47958cos(dectime) + 0.26367dectime	49
North Fork Skokomish River (2)	4.5	0.4 (8.9)	24	$\frac{8.5}{(4.9)}$	MLE: ln(dload)=2.1867 + 0.87207ln(Q) - 0.29034sin(dectime) + 0.24506cos(dectime) + 0.63633dectime	73
Lower Nooksack River (3)	43	3.3 (7.7)	-9.3	<u>76;</u> 70 (-8.8)	MLE: ln(dload)=5.2051 + 1.0989ln(Q)	56
Fishtrap Creek (4)	¹ 2.0	¹ 0.4 (20)	5.0	<u>4.0;</u> 3.2 (-22)	MLE: $\ln(dload)=1.8405 + 1.7693\ln(Q) + 0.24331\ln(Q)^2$	41
Upper Nooksack River (5)	² 6-40	_	-	28;- (-)	_	86
Duwamish River (6)	44	5.1 (12)	51	<u>67;</u> 70 (4.5)	MLE: $\ln(dload)=5.1664 + 1.05\ln(Q)$ + 0.11638 $\ln(Q)^2$	10
Springbrook Creek (7)	1.3	0.2 (15)	28	<u>1.96;</u> 2.0 (3.5)	MLE: ln(dload)=1.8423 + 0.93975ln(Q) + 0.26336sin(dectime) - 0.23241cos(dectime)	2.7
Big Soos Creek (8)	2.9	0.4 (14)	44	<u>3.1;</u> 4.0 (31)	MLE: ln(dload)=2.6321 + 0.66256ln(Q) - 0.15966sin(dectime) + 0.31885cos(dectime)	17
Newaukum Creek (9)	14	2.9 (21)	130	<u>20;</u> 21 (4.5)	MLE: ln(dload)=3.823 + 1.5027ln(Q)	2.8
Upper Green River (10)	0.7	0.08 (11)	44	<u>0.66;</u> 0.73 (11)	MLE: ln(dload=1.1239 + 0.828613ln(Q)	38
Thornton Creek (11)	¹ 0.38	¹ 0.03 (7.9)	20	<u>0.45;</u> 0.44 (-2.6)	MLE: ln(dload)=0.49122 + 0.99741ln(Q) - 0.22626sin(dectime) - 0.22208cos(dectime)	0

¹Calculated from load estimates for the complete water years 1997 and 1998 only.

²Beale ratio estimate (Crawford, 1996).

 Table C4.
 Suspended-sediment loads, standard deviations, and regression equations for load estimates for surface-water sites in the Puget Sound Basin study unit, Washington

[Annual load; Annual load, from the regression equation for the simulation period (10/01/95 - 09/30/98); calculated as annual load, in tons = annual average load, in pounds per day, times 365 days, divided by 2000. Average percentage of difference between measured and predicted daily loads: Measured daily loads, in pounds, are calculated by multiplying the constituent concentration and instantaneous or daily streamflow measured on the day of sample collection. Predicted daily loads, in pounds, are the regression-equation results for the days of sample collection. Measured and predicted loads: Measured load, in tons per year, is estimated by multiplying the simple average of the measured daily loads by 365 days. Predicted load, in tons per year, is estimated by multiplying the simple average of the measured daily loads by 365 days. Precentage of difference = [(predicted - measured)/measured] * 100; ln, natural logarithm; Q, streamflow in cubic feet per second; sin, sine; cos, cosine; dectime, time in fractional years; --, no value; MLE, maximum likelihood estimate; LAE, linear attribution estimate; dload, in pounds]

Site name (Site No.)	Annual load (tons)	Annual load standard deviation, in tons, and (as percentage)	Average percentage of difference between measured and predicted daily loads (pounds)	<u>Measured</u> and predicted loads, in tons per year, and (percentage of difference)	Regression equation	Censored data (percent)
Skokomish River (1)	570,000	270,000 (48)	284	<u>1,500,000;</u> 2,700,000 (85)	MLE: ln(dload) = 11.723 + 2.8062ln(Q)	9
North Fork Skokomish River (2)	14,000	6,400 (46)	80	<u>37,000;</u> 49,000 (31)	MLE: ln(dload)=8.3856 + 2.2075ln(Q) + 0.39712ln(Q) ² - 0.57326sin(dectime) - 0.076696cos(dectime)	27
Lower Nooksack River (3)	1,800,000	310,000 (17)	37	<u>6,400,000</u> : 7,000,000 (9.4)	MLE: ln(dload)=14.266 + 3.2984ln(Q) - 0.30232ln(Q) ² - 0.36187sin(dectime) - 0.25892cos(dectime)	0
Fishtrap Creek (4)	¹ 4,700	¹ 800 (17)	46	<u>8,900;</u> 7,600 (-14)	MLE: $\ln(dload)=9.4784 + 2.0258\ln(Q) + 0.17579\ln(Q)^2$	0
Upper Nooksack River (5)	2,300,000	420,000 (19)	93	7,000,000; 5,900,000 (-16)	² LAE: ln(dload)=13.745 + 4.0916ln(Q) - 0.53322ln(Q) ² + 0.092885sin(dectime) - 0.45368cos(dectime)	0
Duwamish River (6)	270,000	60,000 (22)	82	<u>520,000;</u> 680,000 (30)	LAE: $\ln(dload)=12.6 + 1.8916\ln(Q) + 0.33201\ln(Q)^2$	0
Springbrook Creek (7)	1,800	350 (19)	11	<u>4,800;</u> 4,300 (-9.9)	² LAE: ln(dload)=8.6289 + 1.6051ln(Q)	0
Big Soos Creek (8)	13,000	7,300 (56)	171	<u>12,000;</u> 23,000 (88)	MLE: ln(dload)=9.272 + 2.4213ln(Q)	9
Newaukum Creek (9)	2,200	570 (26)	79	<u>3,400;</u> 3,100 (-6.7)	LAE: ln(dload)=8.2517 + 1.7659ln(Q) + 0.51568sin(dectime) + 0.169cos(dectime)	3
Upper Green River (10)	³ 510	6,200 (>100)	63	<u>270;</u> 220 (-19)	MLE: ln(dload)=6.1389 + 1.4796ln(Q)	19
Thornton Creek (11)	¹ 530	¹ 170 (32)	220	<u>2,200;</u> 1,200 (-48)	² LAE: ln(dload)=6.5066 + 1.8007ln(Q)	2

¹Calculated from load estimates for the complete water years 1997 and 1998 only.

²Regression equation calibrated with instantaneous streamflow (parameter 00061) in place of daily streamflow (parameter 00060).

³Load estimate based on data set excluding a large concentration outlier measured in October 1997.

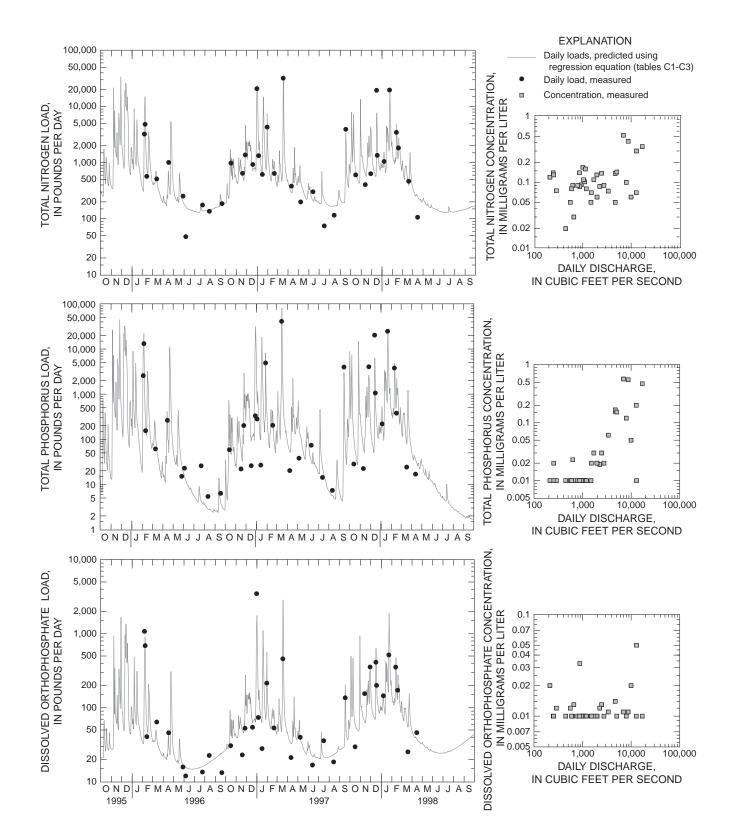


Figure C1. Predicted and measured daily nutrient loads, and scatterplots of nutrient concentrations and streamflows used to calibrate the load-estimate regression equations for the Skokomish River (site 1).

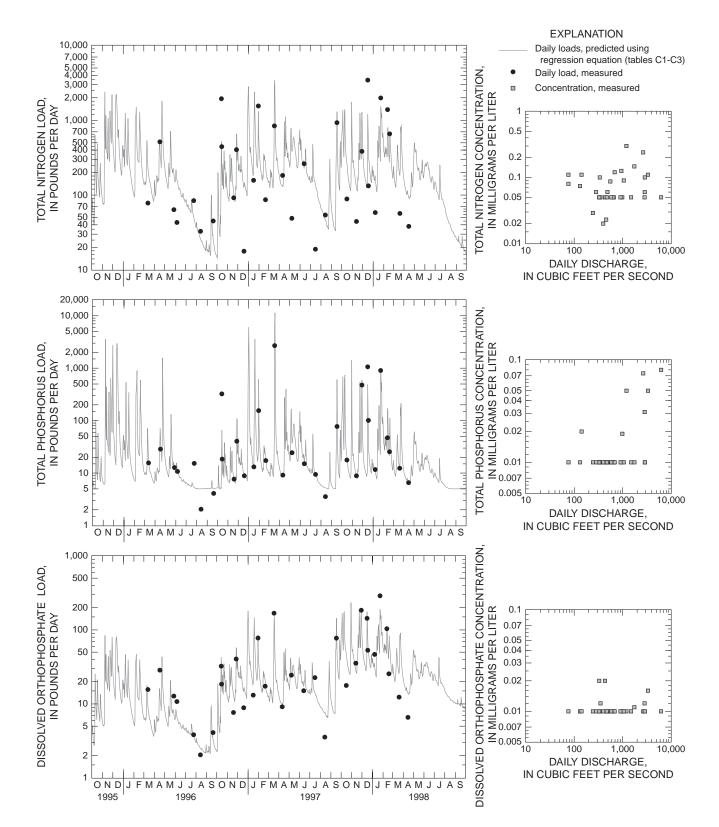


Figure C2. Predicted and measured daily nutrient loads, and scatterplots of nutrient concentrations and streamflows used to calibrate the load-estimate regression equations for the North Fork Skokomish River (site 2) in the Puget Sound Basin study unit, Washington.

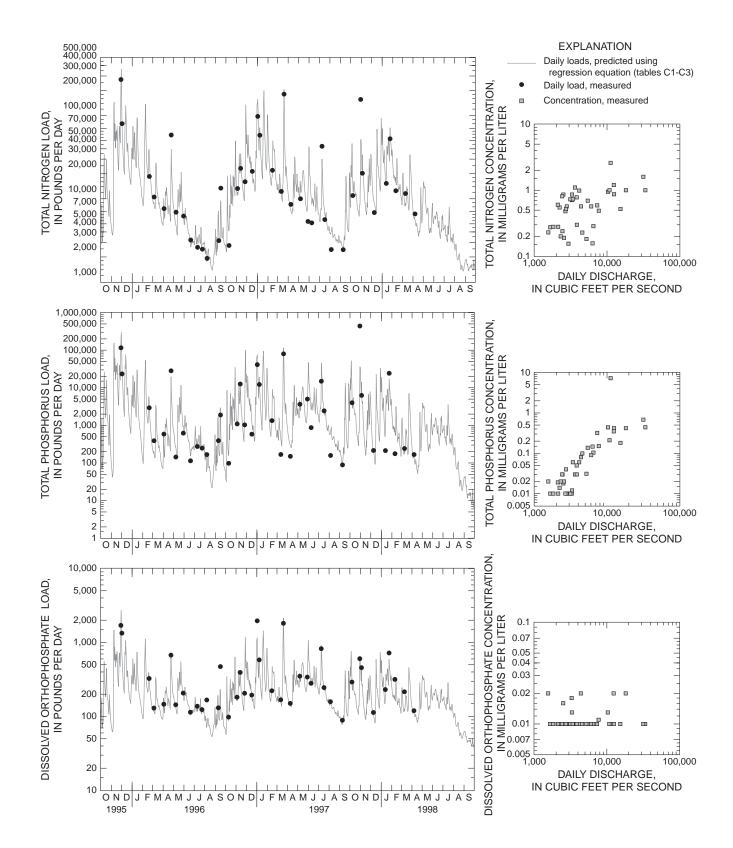


Figure C3. Predicted and measured daily nutrient loads, and scatterplots of nutrient concentrations and streamflows used to calibrate the load-estimate regression equations for the lower Nooksack River (site 3) in the Puget Sound Basin study unit, Washington.

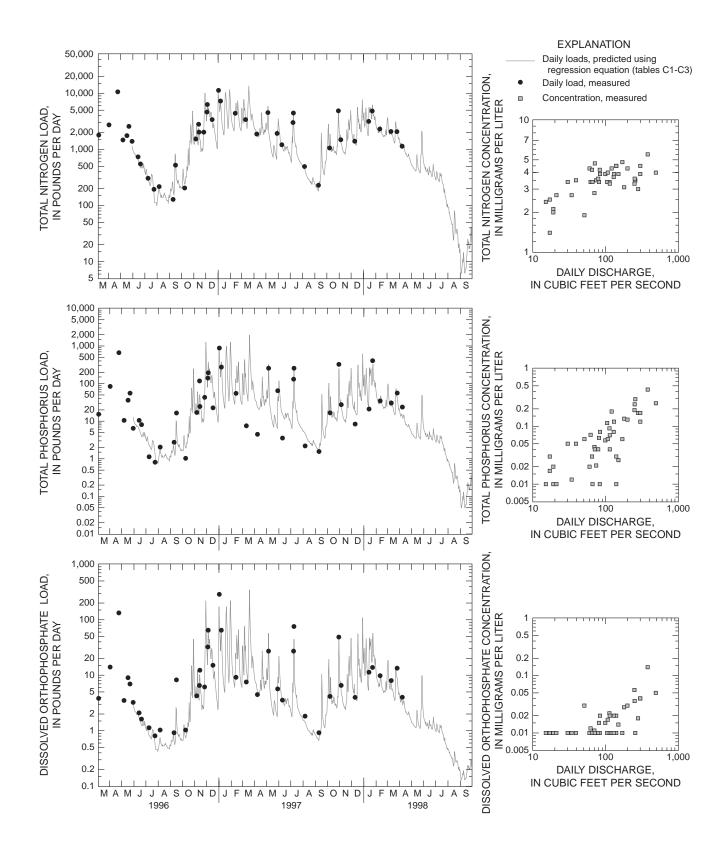


Figure C4. Predicted and measured daily nutrient loads, and scatterplots of nutrient concentrations and streamflows used to calibrate the load-estimate regression equations for Fishtrap Creek (site 4) in the Puget Sound Basin study unit, Washington.

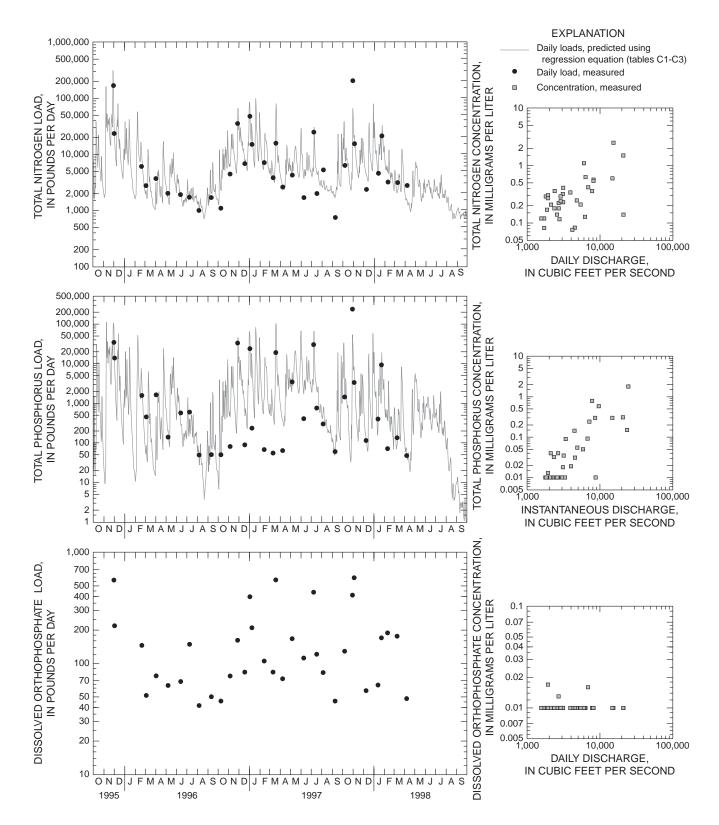


Figure C5. Predicted and measured daily nutrient loads, and scatterplots of nutrient concentrations and streamflows used to calibrate the load-estimate regression equations for the upper Nooksack River (site 5) in the Puget Sound Basin study unit, Washington.

(Daily loads for dissolved orthophosphate phosphorus could not be calculated by the regression method because more than 80 percent of the data were censored at the minimum reporting level).

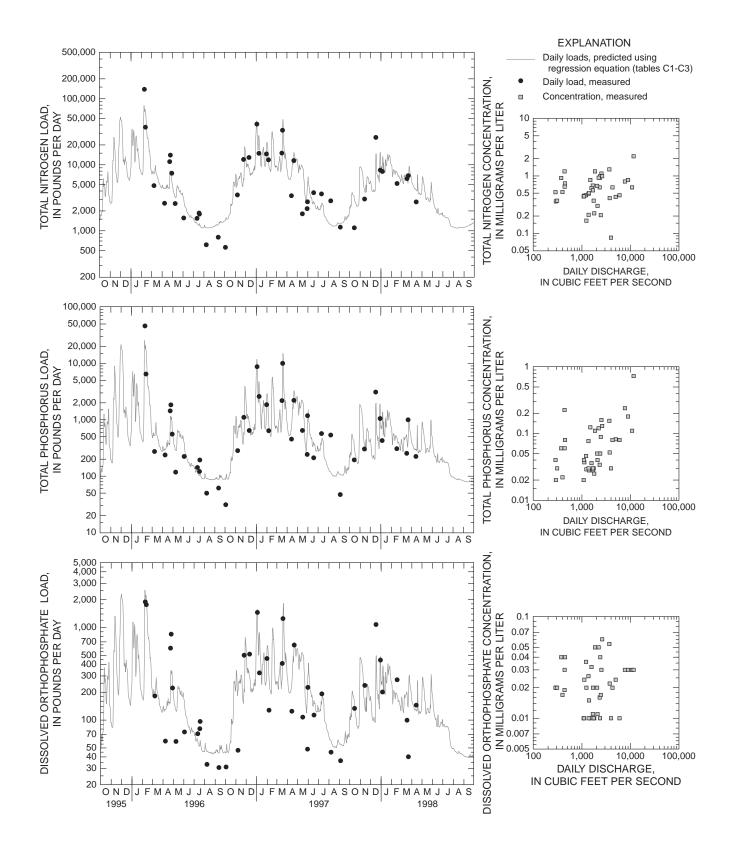


Figure C6. Predicted and measured daily nutrient loads, and scatterplots of nutrient concentrations and streamflows used to calibrate the load-estimate regression equations for the Duwamish River (site 6) in the Puget Sound Basin study unit, Washington.

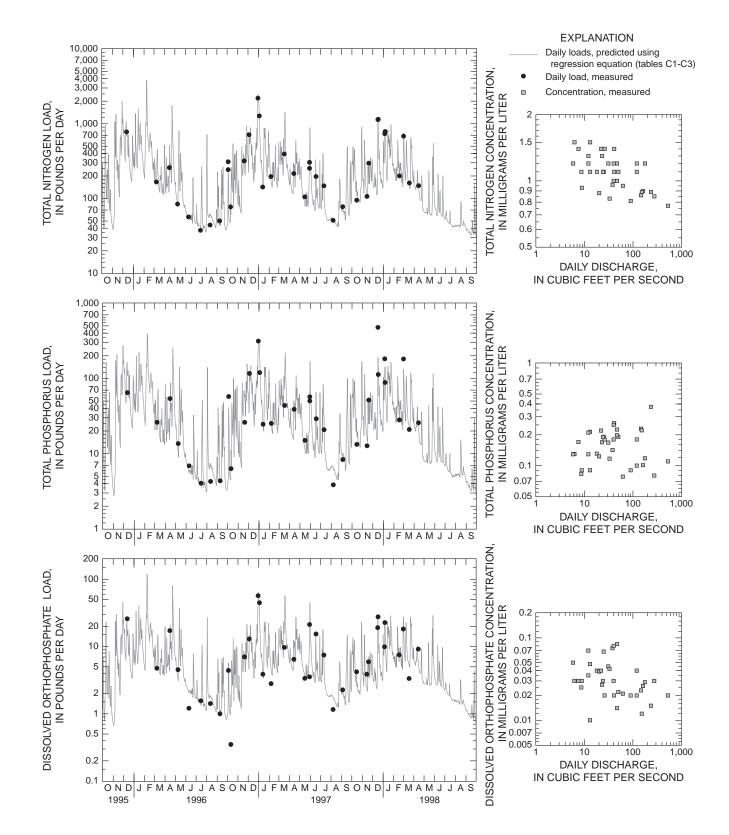


Figure C7. Predicted and measured daily nutrient loads, and scatterplots of nutrient concentrations and streamflows used to calibrate the load-estimate regression equations for Springbrook Creek (site 7) in the Puget Sound Basin study unit, Washington.

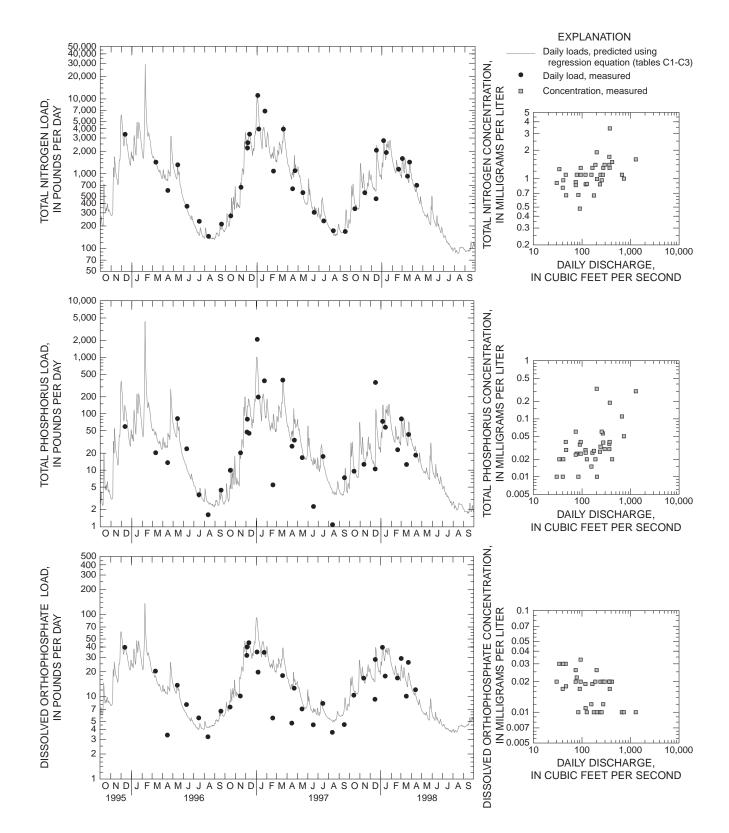


Figure C8. Predicted and measured daily nutrient loads, and scatterplots of nutrient concentrations and streamflows used to calibrate the load-estimate regression equations for Big Soos Creek (site 8) in the Puget Sound Basin study unit, Washington.

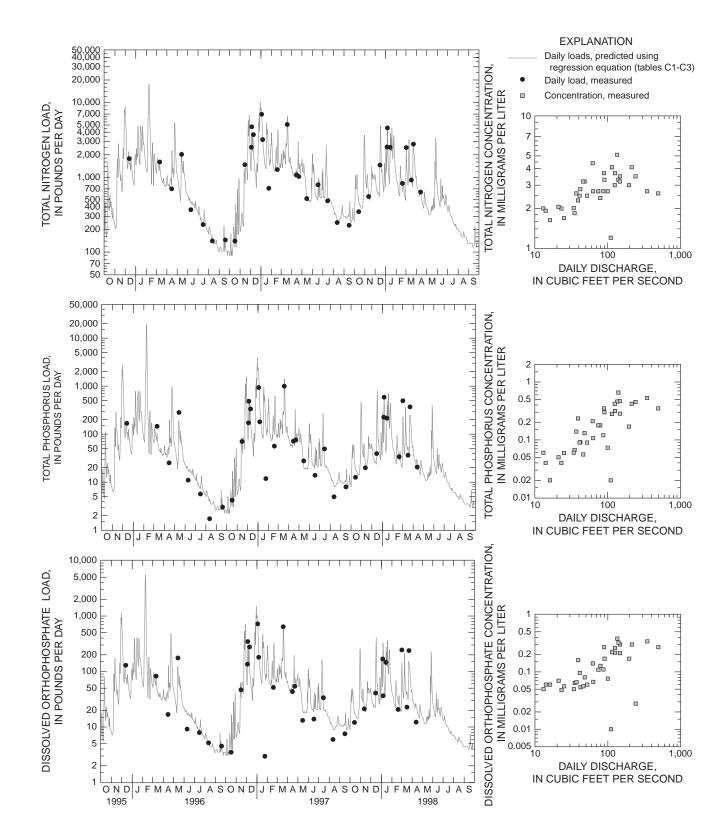
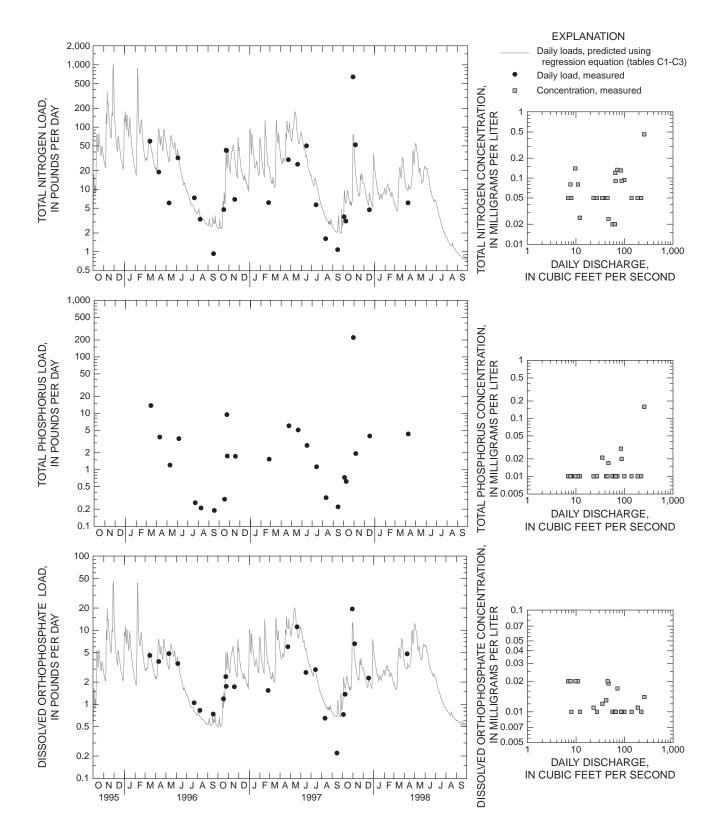
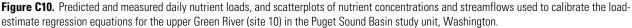


Figure C9. Predicted and measured daily nutrient loads, and scatterplots of nutrient concentrations and streamflows used to calibrate the loadestimate regression equations for Newaukum Creek (site 9) in the Puget Sound Basin study unit, Washington.





(Daily loads for total phosphorus could not be calculated by the regression method because 75 percent of the data were censored at the minimum reporting level).

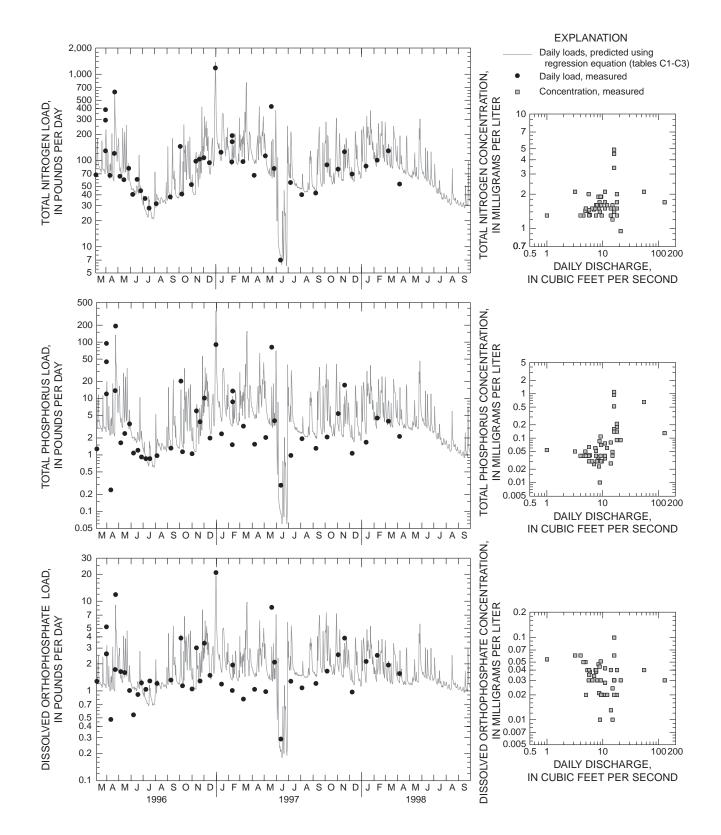


Figure C11. Predicted and measured daily nutrient loads, and scatterplots of nutrient concentrations and streamflows used to calibrate the loadestimate regression equations for Thornton Creek (site 11) in the Puget Sound Basin study unit, Washington.

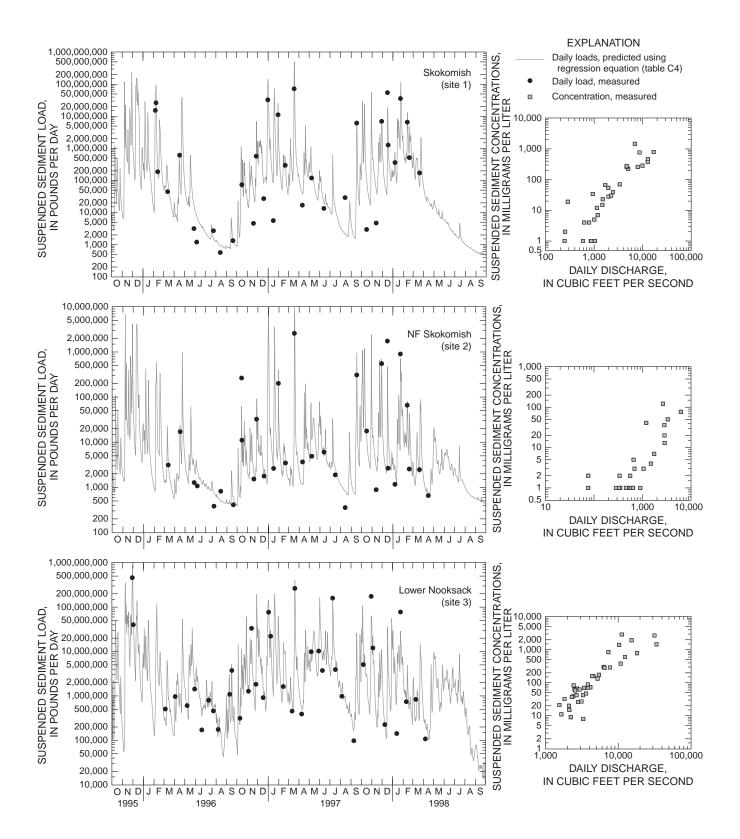


Figure C12. Predicted and measured daily suspended sediment loads, and scatterplots of concentrations and streamflows used to calibrate the load-estimate regression equations for the Puget Sound Basin study unit, Washington.

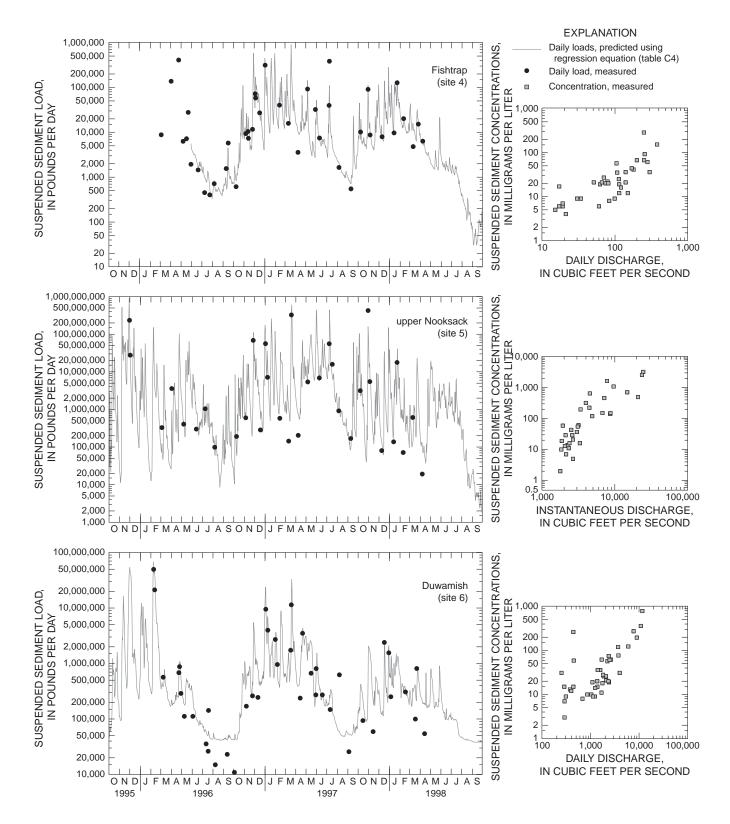


Figure C12. —Continued.

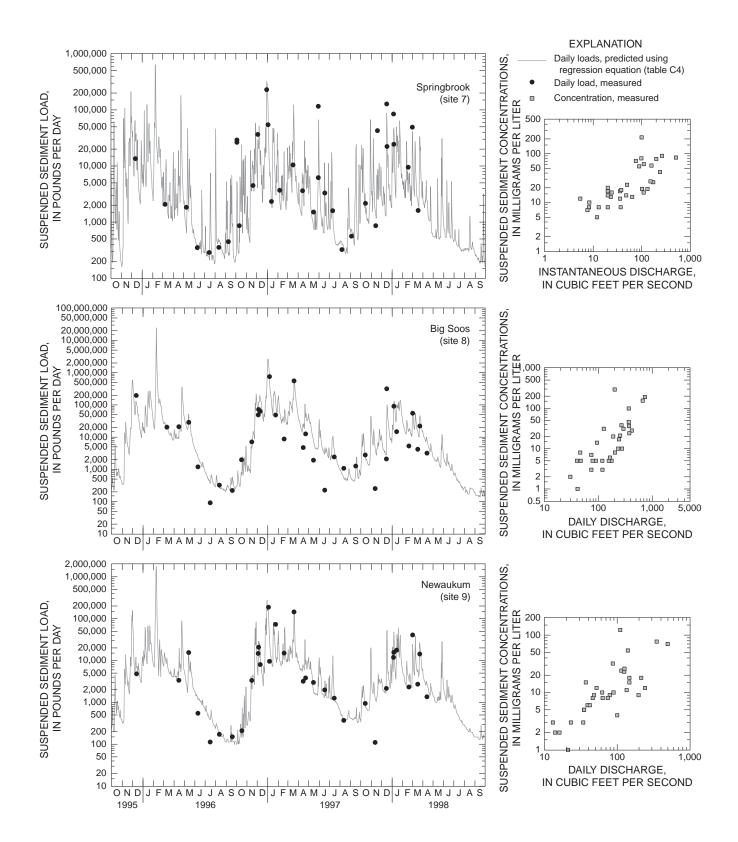


Figure C12. —Continued.

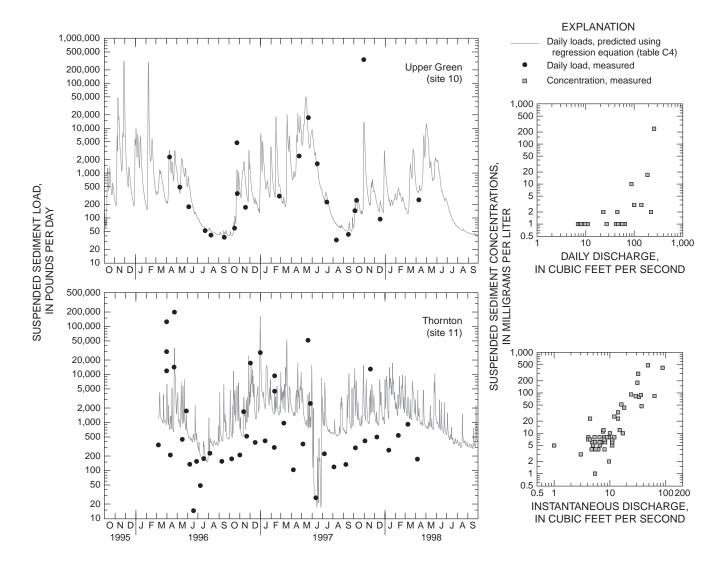


Figure C12. —Continued.

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